R. L. DUTTA

Inorganic Chemistry

Part-II Chemical Elements and their Compounds

THE NEW BOOK STALL

Inorganic Chemistry

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Inorganic Chemistry

R L Dutta

Revised and Enlarged Third Edition

S. C. E. R. T.
Library
Calcutta

THE NEW BOOK STALL
5/1 Ramanath Majumdar Street
Calcutta 700009

Published by
MOHENDRANATH PAUL
The New Book Stall
5/1 Ramanath Majumdar Street
Calcutta 700009

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S.C.E.R.T. W.B. LIBRARY
Date 1.11.99
Accn. No. 9910

Price: Rs. 70·00

First Edition 1973
Second Edition 1981
Reprint 1986
Third Edition 1989

Printed by
Debdas Nath, M A, L-L B
at Sadhana Press Private Ltd
76 B B Ganguli Street
Calcutta 700012

Those sciences are vain and full of errors
which are not born from experiment,
the mother of all certainty.

Leonardo da Vinci (1452-1519)

Preface to the Third Edition

All the Chapters have been thoroughly revised and updated. Substantial amount of new materials have been added to the lanthanides, organometallics, unusual oxidation states of the transition elements and flexidentate behaviour of polydentate ligands. Discussion on the electronic spectra of coordination complexes of transition elements are a natural follow-up of the theoretical background developed in Chapter 11 of Part I of the book. It is hoped that this revised and enlarged third edition will be of better service to the users of the book.

The delay in the publication of this revised edition is sincerely regretted. I take the opportunity of thanking all the students and teachers who have taken a keen interest in the book and have so kindly forwarded their valued comments and suggestions for further improvement.

R L DUTTA

Santiniketan
Birbhum, West Bengal
August 1989

Preface to the Second Edition

The second part of the book Inorganic Chemistry deals with the Chemical Elements and their Compounds. In response to pressing demands from many quarters enough descriptive matter has been added in all the Chapters. As a teacher I have always abhored presenting too much of factual chemistry alongside too little of basic principles. I have therefore endeavoured to strike a balance between principles and facts. The revisions done in Part II have been designed to be in tune with the principles presented in Part I. Several appendices at the end are expected to be useful to the young readers.

It is a pleasure to express my heartfelt thanks to my research associates Shri R Sharma and Md Munkir Hussain for their assistance in proof reading. I am grateful to Shri Debdas Nath and Shri Mohendra Nath Paul for the competence and patience with which they have attended to many last minute changes in the manuscript and in the proofs, that I had asked for.

Finally I take this opportunity of thanking all the students and teachers who have so kindly sent in their valued comments and suggestions on the first edition. Further suggestions for improvement are welcome.

R L DUTTA

Burdwan, West Bengal
June 1981

Preface to the First Edition

The book is designed to serve mainly B Sc (Honours) undergraduates of Indian Universities. Some chapters will be useful to M Sc students as well. An endeavour has been made to show that the properties of chemical elements are closely related to their electronic configuration. Orbital hybridisation, molecular orbital and crystal field models have been introduced for a clear understanding of modern inorganic chemistry. Study questions and bibliography are added after each chapter.

I am thankful to Dr S C Rakshit, Dr A K Chaudhury, Dr A S Basu, Dr G S De, Shri G P Sengupta and Shri S Sarkar for their comments. I am particularly grateful to Dr S Ghosh for going through the manuscript and making useful suggestions on the draft. I am also thankful to the management and staff of M/S. Sadhana Press Pvt. Ltd for their cooperation. I wish to record my deep sense of gratitude to Prof. S R Palit for encouragement but for which the book would not have seen the light of the day.

Despite my best efforts, some errors might have crept in. Suggestions and criticisms from learned professors and inquisitive students towards improvement will be thankfully received and gratefully acknowledged in the next edition.

R L DUTTA

Burdwan, West Bengal
June 1973

Abbreviations

Å, Angstrom unit, 10^{-8} cm
acacH, acetylacetone
B, Racah interelectronic repulsion parameter
B′, Racah interelectronic repulsion parameter in complexes
Bigh, biguanide
B.P., boling point
BPHAH, N-benzoyl N-phenylhydroxylamine
BPOH, 2-benzoylpyridine oxime
B.M., Bohr Magneton
CFSE, crystal field stabilisation energy
d, dextrorotatory
DAPDH$_2$, diacetyl pyridine dioxime
diars, o-phenylene bisdimethylarsine $C_6H_4(As(CH_3)_2)_2$
dien, diethylenetriamine
diglyme, diethyleneglycoldimethylether
dipy, -dipyridyl
DMGH, dimethylglyoxime
DMSO, dimethylsulphoxide
E.A., electron affinity
EDTAH$_4$, ethylenediaminetetraacetic acid
en, ethylenediamine
e.v., electron volt
h, Planck‘s constant
IDAH$_2$, iminodiacetic acid
I.P., ionisation potential
kK, Kilokayser (1kK = 1000 cm^{-1})
l, levorotatory
LCAO, linear combination of atomic orbitals
LutH$_2$, lutidinic acid (pyridine 2, 6 dicarboxylic acid, dipicH$_2$)
MIBK, methylisobutyl ketone

M.O., molecular orbital
M.P., melting point
$m\mu$, millimicron (10A)
NicH, nicotinic acid
nm, nanometre (millimicron)
$OPPh_3$, triphenyl phosphine oxide
OxH_2, oxalic acid
OxinH, 8-hydroxyquinoline
o-phen, o-phenanthroline
PicH, picolinic acid
PPh_3, triphenylphosphine
py, pyridine
QAS, tris (o-phenylarsinophenyl) arsine
QH, quinaldinic acid
salglyH, salicylideneglycine
SBH_2, dibasic tridentate Schiff base
$tartH_2$, tartaric acid
TBP, tributylphosphate
THF, tetrahydrofuran
VB, valence bond
χ magnetic susceptibility
μ, magnetic moment in B.M.
ϵ, molar extinction coefficient
λ_{max} wave length of maximum absorption

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PART II

THE CHEMICAL ELEMENTS AND THEIR COMPOUNDS

13

Group IA. Hydrogen

Hydrogen occupies a unique position among the chemical elements. In its diatomic molecular form, H_2, it occurs in our atmosphere to a minute extent, only one part in a million by volume. But in the form of naturally occurring water its abundance is about 0.9% by weight.

Ignoring the noble gas helium, hydrogen is unique among the elements in having one electron in the 1*s* orbital and no other electron shells. Hydrogen is thus invariably monovalent. Because of its similarities both to the alkalies and to the halogens it may be assigned a position either in group IA or in group VIIB. Like the alkalies hydrogen has a single electron in the outer valence shell, and like the halogens it is just one electron short of a noble gas, in this case the $1s^2$ helium. Conventionally, however, hydrogen is placed in group IA. Like the alkalies hydrogen forms a solvated cation, H_3O^+ in water, which on elctrolysis gives hydrogen at the cathode. Like the halogens in alkali halides hydrogen is present as the negative hydride anion in alkali- and alkaline earth hydrides, LiH, CsH, CaH_2 etc, which on electrolysis liberate hydrogen at the anode.

13.1. SALIENT FEATURES OF HYDROGEN CHEMISTRY

Hydrogen assumes several forms in elementary state and plays different roles in different compounds. Following are the salient features of its chemistry:

1. Hydrogen has three isotopes of mass numbers 1, 2 and 3. Although isotopes of a particular element possess basically the same chemistry, the isotopes of hydrogen shows considerable variation in their physical properties due to a wide variation in mass numbers. Because of such wide variations the three isotopes have been given separate names: *protium* (commonly called hydrogen), *deuterium* and *tritium*. Naturally occurring hydrogen contains a small amount of deuterium whereas tritium is known only as a product of artificial transmutation or as a product of cosmic ray-induced nuclear reaction in the upper atmosphere.

II. Elementary hydrogen is found to occur in the following forms: (*a*) Diatomic molecular form of hydrogen exists in two varieties resulting from the spins of the two nuclei being in the same direction (*ortho hydrogen*) or the spins of the two nuclei being in opposite direction (*para hydrogen*). Ortho and para isomers are thus nuclear spin isomers. Deuterium is also known in two nuclear spin forms. (*b*) Under certain conditions the molecular form may be forced to form monatomic, active hydrogen.

III. In chemical combination with other elements hydrogen shows the following features: (*a*) It is present in acids as H^+, being the result of the loss of the valence electron of hydrogen atom. H^+, being a bare proton, has an enormous polarising power and therefore exists in solvents as a solvated proton (Chapter 8). The proton is also produced by electric discharge through hydrogen, and also in certain nuclear reactions. (*b*) In alkali metal- or alkaline earth hydrides, hydrogen is present in the anion as H^-. This is a consequence of gaining one electron from the electropositive metals. Hydrogen thus assumes the helium electronic configuration. (*c*) In hundreds of compounds hydrogen forms single shared-pair covalent bonds (e.g. CH_4, NH_3). (*d*) In highly polar hydrides such as H_2O, HF, NH_3 there is considerable association through hydrogen bonding. (*e*) In electron deficient molecules like boron hydrides it forms hydrogen-bridge bond leading to three-centred two-electron bonds, instead of the usual two-centred two-electron bonds.

13.2. ISOTOPES OF HYDROGEN

Hydrogen has three isotopes: protium, deuterium and tritium (Table 13.1). Properties of pure protium and its compounds are identical with those of the natural isotopic mixture. The properties of deuterium are distinct enough to merit separate discussion. In this context it should be realised that one unit mass difference would hardly bring about any distinctive change in properties of isotopes in the case of heavy elements. The relative difference in the masses of protium and deuterium is large enough to cause some distinctive variation in their physical properties.

Table 13.1. The three Isotopes of Hydrogen

Characteristic	Hydrogen (Protium)	Deuterium	Tritium
Symbol	H	D	T
Mass Number	1	2	3
Number of Protons	1	1	1
Number of Neutrons	0	1	2
Atomic Weight (C-12 scale)	1.007829	2.014199	3.016049
Percent Abundance	99.9844	0.0156	10^{-15}

Common methods of isotope separation namely diffusion, thermal diffusion, evaporation are not of as much merit as electrolysis is for the separation of deuterium from protium. If water containing protium and deuterium is electrolysed the gas evolved at the cathode has a smaller deuterium/protium(hydrogen) ratio than the residual water. Progressive electrolysis leads to concentration of deuterium in the electrolytic cell. For details see Chapter 12.

By virtue of its larger mass deuterium reacts slower than protium. Those physical properties, which are mass dependent, are different for protium and deuterium, and their compounds. Some such properties are included in Table 13.2.

Table 13.2. Physical Properties of H_2, D_2, H_2O and D_2O

Property	H_2	D_2	H_2O	D_2O
Melting Point (°C)	−259.2	−254.5	0	3.82
Boiling Point (°C)	−252.7	−249.5	100	101.4
Specific Gravity (20°C)			0.9982	1.1059
Temperature of Maximum Density			4.08	11.2
Latent Heat of Fusion (Cal/mole)	28	52		
Viscosity (millipoise) 20°C)			10.09	12.6
Ionic Mobility (K^+) × 10^5 (cm/sec/volt at 18°C)			64.2	54.5
Ionic Mobility (H^+ or D^+ in respective solvents) × 10^5 (cm/sec/volt at 18°C)			315.2	213.7

Because of similar chemical behaviour of isotopes, syntheses of deuterium compounds are like corresponding hydrogen compounds. Deuterium combines directly with halogens to form deuterohalides. Deuterium oxide, called *heavy water*, reacts with acid anhydrides, SO_3, N_2O_5, P_2O_5 etc. to form the corresponding (heavy) deutero acids D_2SO_4, DNO_3, D_3PO_4 etc. Under suitable experimental conditions hydrogen atoms in organic compounds can be exchanged for deuterium. With platinum black as catalyst the reaction between benzene and deuterium leads to deuterobenzene (heavy benzene): $C_6H_6 + 3D_2 \rightleftharpoons C_6D_6 + 3H_2$. Repeated crystallisation of some compounds from D_2O also results in deuterium being exchanged for the hydrogen.

Heavy water is an associated liquid with *deuterium bond* between individual D_2O molecules. The electronegativity difference between oxygen and deuterium makes oxygen negative ($\delta^-\delta^-$) and deuterium positive (δ^+). Dipolar attraction then leads to association. D_2O finds application in nuclear reactors as a moderator of fission neutrons. D_2O has stable nuclei which do not react with neutrons and hence is useful in slowing down the speed of the fast neutrons. D_2O is also used in hydrogen exchange reactions in chemical research studies. For example, on deuteration of a compound containing $=NH$ to $=ND$, the $=NH$ frequency in the infra red spectrum will vanish and a new band at lower energy characteristic of $=ND$ will appear.

Tritium is a rare isotope of hydrogen. Several types of nuclear reactions lead to its synthesis. Bombardment of lithium by slow neutrons produces tritium. The tritium is removed from helium by absorption on uranium metal as UT_3

$$^{6}_{3}Li + ^{1}_{0}n \rightarrow ^{4}_{2}He + ^{3}_{1}H$$

and the tritium separated by heating UT_3 at 500°C. Bombardment of beryllium with deuterium nucleus (deuteron) also produces tritium.

$$^{9}_{4}Be + ^{2}_{1}D \rightarrow 2\ ^{4}_{2}He + ^{3}_{1}H$$

The trace quantity of tritium that is found in nature is formed in the nuclear reactions initiated by fast neutrons arising from cosmic ray reactions:

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{12}_{6}C + ^{3}_{1}H$$

Tritium is a beta emitter with a half life of 12.4 years and thus helium-3 is produced:

$$^{3}_{1}H \rightarrow ^{3}_{2}He + ^{0}_{-1}e$$

The hydrogen isotopes need not be confused as *allotropes*. Allotropes have commonly been defined as different structural forms of the same element, that exist in the same physical state. Common examples of allotropes are (*a*) diamond and graphite (*b*) red and white phosphorus (*c*) diatomic molecular oxygen, O_2, and triatomic ozone, O_3. Isotopes are also different forms of atoms of the same element but they cannot give rise to different structural forms in the elementary state. Isotopic species involve a difference in the composition of their nuclei alone but the behaviour of the extranuclear electrons remains the same. On the contrary, in allotropes different structural forms must originate from a difference in the bonding pattern of the extranuclear electrons. Diamond, for example, has sp^3 hybridised tetrahedral carbon whereas in graphite all carbon atoms are sp^2 hybridised (Chapter 17). On the other hand molecular protium, H_2, has a single covalent link due to the overlap of the 1*s* orbitals of the two H atoms. Molecular deuterium, D_2, has also the same covalent link. The only change in the two isotopic forms, H_2 and D_2, occurs in their nuclei.

13.3. ORTHO AND PARA HYDROGEN

In the covalent link between the two hydrogen atoms forming H_2 molecule the electron spins are opposed following Pauli principle. The two nuclei (protons), however, have the freedom of spinning in the same direction or in opposite direction (Fig.13.1). The symmetrical para form has a lower energy than the ortho form, so that increasing temperature favours the conversion of the para form to the ortho form. Near absolute zero molecular hydrogen consists entirely of the para form but at elevated temperature an equilibrium is attained with three moles of ortho to one of para form. This equilibrium mixture makes up

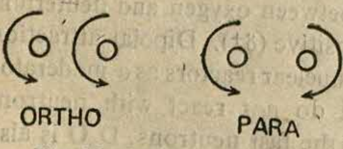

FIG. 13.1. Ortho and para hydrogen

ordinary molecular hydrogen at room temperature. The equilibrium cannot be shifted entirely in favour of ortho hydrogen. However, conversion of ortho hydrogen to para hydrogen is catalysed by Cr_2O_3, Gd_2O_3 and Pr_2O_3. The paramagnetism of these oxides seems to influence the nuclear spin alignment of the hydrogen molecule.

Since both the para and ortho hydrogen possess the same covalent bonding their chemical behaviour is the same. There exist slight variations only in their physical properties such as thermal conductivity. This difference in thermal conductivity is utilised in the analysis of ortho-para mixture by measuring the loss of heat of a wire heated to around 160°K in the mixture to be analysed.

The existence of ortho and para forms has also been established in deuterium. Molecular deuterium is composed of two parts ortho and one part para form at ordinary temperature. Due to the different spins of the nucleus, unlike hydrogen, ortho deuterium has lower energy and the para deuterium has higher energy.

Once again it should be noted that the ortho and para forms of hydrogen do not involve any difference in the chemical bonding between the two hydrogen atoms. Hence they cannot be called allotropes. The ortho and para forms may be viewed as *nuclear spin isomers*.

13.4. ATOMIC HYDROGEN

Molecular hydrogen can be dissociated into atomic form in more than one way: (*a*) Wires of tungsten, platinum or palladium at 1000–2000°C absorb molecular hydrogen at 0.01 mm. pressure but emit atomic hydrogen. (*b*) Molecular hydrogen is also atomised when it is bombarded by slow neutrons. (*c*) Electric discharge through hydrogen at a fraction of a millimetre pressure also leads to atomisation.

Atomic hydrogen is very short lived. The huge amount of heat of recombination ($H + H = H_2 + 103.4$ Kcals) was utilised by Langmuir in his atomic blow-pipe for welding purposes. A stream of highly atomised hydrogen is directed on the metal plate to be welded. The metal serves as the third body and helps dissipating the heat of recombination of the hydrogen atoms. This atomic blow-pipe has the further advantage that it maintains a reducing atmosphere during welding.

Atomic hydrogen is a very strong reducing agent. It converts oxygen to H_2O_2, reduces ethylene to ethane. Aqueous solutions of silver nitrate, mercuric chloride and cupric acetate are reduced to the corresponding metals. Permanganate and chromate ions are reduced to manganous and chromic ions respectively. Sulphur, chlorine, bromine and iodine are rapidly converted to their hydrides. Carbon dioxide is converted to formic acid.

13.5. BINARY HYDRIDES

Binary compounds of hydrogen with other elements are known as hydrides. Strictly speaking the term should apply only to those binary compounds which have hydrogen in the anion. But the common practice is to use the term in a general sense. The binary hydrides may be classified into three principal categories according to the type of bonding, physical and chemical behaviours: (*a*) ionic hydrides, (*b*) covalent hydrides and (*c*) transition metal hydrides.

13.5.1. Ionic Hydrides: These are variously called as ionic hydrides, electrovalent hydrides, saline hydrides or as salt-like hydrides. All these names, however, point to one common aspect that the bonding in these binary hydrides is predominantly ionic. In these compounds hydrogen is present as a negatively charged hydride ion, H^-. It is formally analogous to a halide ion. It can be guessed that elements with low ionisation potential will form this type of hydrides. The alkalies and the alkaline earths have the lowest first ionisation potentials whereas hydrogen has a far larger value. Also note that both hydrogen and the alkalies have close electron affinities but their electronegativities vary considerably. Considering all these aspects it is logical to predict that in the hydrides of the strongly electropositive metals hydrogen will assume the role of an anion.

	H	Li	Na	K	Rb	Cs	Ca	Sr	Ba
First I.P. (*e.v.*)	13.59	5.39	5.14	4.34	4.18	3.89	6.11	5.69	5.21
Second I.P. (*e.v.*)	...	...	...	...	...	...	11.87	11.02	10.00
Electron Affinity (*e.v.*)	0.747	0.54	0.74	0.70	...	...	...	...	...
Electronegativity	2.1	1.0	0.9	0.80	0.8	0.7	1.0	1.0	0.9

These compounds are typical ionic compounds with high melting points, high degree of thermal stability and ionic crystal structures. In fused state they conduct electricity and on electrolysis the alkalies or the alkaline earths migrate to the cathode whereas the hydride ion goes to the anode. The salt-like hydrides are the only compounds known, which on electrolysis give hydrogen at the anode.

$$\mathrm{NaH} \xrightarrow[\text{electrolysis}]{\text{fused}} \mathrm{Na^+} + \mathrm{H^-} - \begin{cases} \rightarrow (a) \text{ at the cathode: } \mathrm{Na^+} + e \rightarrow \mathrm{Na} \\ \rightarrow (b) \text{ at the anode: } 2\mathrm{H^-} \rightarrow \mathrm{H_2} + 2e \end{cases}$$

In the long-form Periodic Table the elements forming such ionic hydrides are located at the left hand corner. The only practical method of their preparation is the direct reaction of the alkalies or the alkaline earths with elemental hydrogen at an elevated temperature (300–600°C). It is interesting to note that during the syntheses of the saline hydrides hydrogen performs the role of an oxidising agent (instead of its familiar role as reductant) by extracting electron (s) from the alkali/alkaline earth metals.

An important property of these hydrides is their reducing ability. These hydrides find applications in the syntheses of some organic compounds and free metals, and in the removal of scales from iron :

$$2BF_3 + 6NaH \xrightarrow{200^\circ C} B_2H_6 + 6NaF$$

$$(C_6H_5)_2CO + NaH \xrightarrow{145^\circ C} (C_6H_5)_2CHONa \xrightarrow{H_2O} (C_6H_5)_2CHOH + NaOH$$

$$TiCl_4 + 4NaH \xrightarrow{400^\circ C} Ti + 4NaCl + 2H_2$$

$$2Fe(OH)_3 + 6NaH \longrightarrow 2Fe + 6NaOH + 3H_2$$

With water and liquid ammonia hydrogen is evolved:

$$CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2; \quad LiH + NH_3 \longrightarrow LiNH_2 + H_2$$

Due to the ready synthesis of hydrogen via hydrolysis of LiH and CaH_2, these are often used as suitable replacements of hydrogen cylinders which are heavy and difficult to transport.

13.5.2. Covalent Hydrides. These are often called gaseous or volatile hydrides. The bond type is usually two-centred shared electron pair covalent bond. In special cases, however, three-centred two-electron covalent bonds may be formed. Characteristic of covalent bonds, the elements forming such binary hydrides have high ionisation potentials and their electronegativities are close to that of hydrogen.

	H	B	C	Si	N	P	O	S
First I.P. (*e.v.*)	13.59	8.30	11.26	8.15	14.53	10.48	13.61	10.36
Electronegativity	2.1	2.0	2.5	1.8	3.0	2.1	3.5	2.5

All subgroup B elements of IIIB to VIIB from covalent hydrides:

These elements are located at the right-hand side of the long-form Periodic Table.

IIIB	IVB	VB	VIB	VIIB
B	C	N	O	F
Al	Si	P	S	Cl
Ga	Ge	As	Se	Br
	Sn	Sb	Te	I
	Pb	Bi	Po	

These hyrdides are non-electrolytes, low melting and low boiling. Some general features with respect to their volatility, thermal stability, acidity and reducing ability are enumerated below:

(*a*) In a series of hydrides of the same period the effect of molecular weight on the boiling point may sometimes be masked by factors like polarity. This aspect in the hydrides NH_3, H_2O and HF has been discussed under hydrogen bonding (Chapter 5).

(*b*) In a series of hydrides of the same group the boiling points should increase with molecular weight since the molecular weight differences are now appreciable. NH_3, H_2O and HF are exceptions in the respective groups.

(*c*) There is a general increase in thermal stability from left to right along a period. This is shown by the hydrides of Al, Si, P, S and Cl. The electronegativities of the parent elements increase along a period.

(*d*) There is a general decrease in thermal stability along a group. This is shown nicely by the hydrides of C, Si, Ge, Sn and Pb. Whereas CH_4 can exist in limited quantities in equilibrium with carbon and hydrogen at $> 1000°C$, SiH_4 decomposes irreversibly at $\sim 400°C$ and PbH_4 is unstable at room temperature. This behaviour is due to the increasing X—H distance which leads to a weakening of the covalent bond.

(*e*) Of two elements of similar electronegativity but of different size, the one with larger size invariably forms the less stable hydride. Thus CH_4 is more stable than H_2S, PH_3 more stable than TeH_2, and SiH_4 more stable than SbH_3.

(*f*) Along a group with increasing atomic number the bond length (X—H) increases and the hydrogen tends to dissociate more readily. So the acidity increases with increasing atomic number: $H_2Te > H_2Se > H_2S > H_2O$.

(*g*) Reducing properties of the covalent hydrides increase with increasing atomic number along a group. For example, H_2S and H_2Se are better reducing agents than H_2O, and H_2Te still better than H_2S and H_2Se. This enhanced reducing ability must be connected with the case of dissociation of the H—X acids with increasing atomic number of X.

Some general methods of syntheses may be pointed out.

(1) Direct reaction of hydrogen with the parent element often gives the hydrides (NH_3, H_2O etc.), the exact condition depending on the hydride.

(2) Certain binary compounds readily react with aqueous acids or water alone to form the hydrides of their non-metallic parents:

$$Mg_2Si + 4HCl \rightarrow SiH_4 + 2MgCl_2$$
$$Ca_3P_2 + 6H_2O \rightarrow 2PH_3 + 3Ca(OH)_2$$

(3) Electrolytic reactions have also been used to synthesise hydrides of the heavier and more metallic elements in the covalent hydride group. While the H^+ ions are discharged on the cathode there may occur some reaction between the cathode metal and hydrogen to produce a volatile hydride. For example, SbH_3 can be obtained by the electrolysis of acid or alkaline solutions employing a cathode of metallic antimony.

(4) Metathetical reactions with some ionic hydrides in suitable solvents may also provide covalent hydrides:

$$3LiH + AlCl_3 \xrightarrow{\text{ether}} AlH_3 + 3LiCl$$

13.5.3. Transition Metal Hydrides. These are the hydride compounds formed by the transition elements of the central region of the long form Periodic Table. Most of the hydrides in this category cannot be considered as true, stoichiometric chemical compounds. Some typical examples are $TiH_{1\cdot73}$, $VH_{0\cdot6}$, $CeH_{2\cdot8}$ UH_3, $ZrH_{1\cdot9}$. Some of these compounds are merely the results of absorption, occlusion or adsorption of hydrogen by finely divided transition metals. They are mostly interstitial compounds, the small hydrogen atoms occupying some of the holes between the atoms in the transition metal lattice. The nature of the linkage between hydrogen and the metal lattice is not well understood. The capacity of different metals to adsorb, occlude or absorb hydrogen decreases progressively across the Periodic Table from left to right. The lanthanides in group IIIA have the highest ability of absorbing hydrogen (LaH_3). Elements of group VIII (with the exception of palladium) are relatively innocent to hydrogen absorption. During hydrogen absorption or occlusion there is some expansion of the metal lattice, so that the hydrides are less dense than the metals. This expansion varies directly with the ability of the elements to absorb hydrogen. Interestingly in ionic hydrides, there is a decrease in volume from the metal to the hydride, that is, an increase in density from metal to its hydride. Absorption of hydrogen by the transition metals generally leads to a decrease of the metallic character of the metal.

Transition metal hydrides are obtained by (1) direct combination of the metal and hydrogen at elevated temperatures (2) by reduction of metal salts by organic reducing agents (3) by absorption of hydrogen by metal cathodes during electrolysis of aqueous as well as non-aqueous solution. Of the elements of group VIII, iron, cobalt and nickel salts give dark, finely divided powders on reduction with organic reducing agents. These dark powders often contain considerable amounts of hydrogen, and often burn in air. They also serve as good catalysts in organic hydrogenation reactions. Palladium metal can absorb and retain a large amount of hydrogen to suggest a formula $PdH_{0.8}$.

We derive an interesting explanation of the loose combination of hydrogen in these interstitial hydrides when we apply radius ratio rules for octahedral/tetrahedral hole fitting of the metallic lattice by hydrogen. For a small atom to effectively fit the octahedral holes created by close packing of bigger atoms the ratio of small atom radius to big atom radius should be within the range 0.41 to 0.73. Taking the case of titanium (atomic radius, 1.47A) the small atom radius should be in the range ~0.60A to 1.03A. For a tetrahedral hole fitting the ratio has to be in the range 0.225 to 0.41 so that for the titanium case the small atom radius should preferably be ~0.33 to 0.60A. Taking the hydrogen covalent radius as 0.28A we find that it will 'rattle' in octahedral/tetrahedral holes of a metallic lattice (Chapter 6; page, 111).

13.6. HYDROGEN BRIDGE BOND

The electron deficient (shortage from an octet) character of trivalent boron in BH_3 leads to its dimerisation to B_2H_6. (There are a host of other electron deficient boron hydrides eg: B_4H_{10}, B_5H_9, B_6H_{10} etc.) Our usual concept of shared-pair bonds does not hold in this compound. Usual single bond representation of its configuration must take care of seven bonds but there are only twelve electrons available instead of fourteen. If two of these seven bonds are conceived as one-electron bonds then diborane, B_2H_6, must be paramagnetic but experiment shows it to be diamagnetic. The problem has been solved by invoking two-electron three-centred bonds. The structure consists of two irregular tetrahedra (with a boron at the centre of each) overlapping with each other at two points. Each boron has roughly four sp^3 hybrid orbitals. Two of these hybrid orbitals overlap with the 1*s* orbitals of two terminal hydrogens. The other two hybrid orbitals of one boron overlap two other hybrid orbitals of the other boron through the 1*s* orbitals of two bridging hydrogens. Thus there are two B—H—B three-centred two-electron bonds. Such bent bonds are popularly called 'banana' bonds (Fig. 13.2 and 13.3).

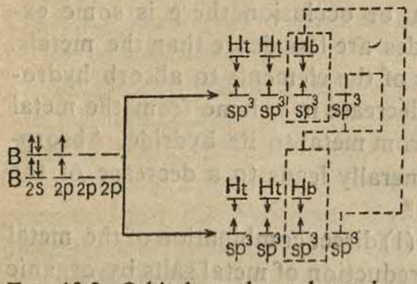

FIG. 13.2. Orbital overlap scheme in B_2H_6:H_t = terminal hydrogen; H_b = bridging hydrogen

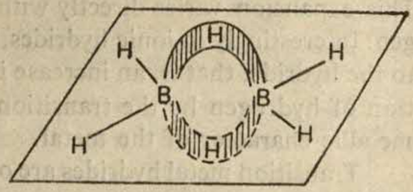

FIG. 13.3. Banana bond in B_2H_6(cf: FIG. 13.2; B—B = 1.77A; H_t—B = 1.19A; $<H_tBH_t$= 121°; $<H_bBH_b$ = 97°;)

For the two two-electron three-centred (B H B) bonds we can have an M.O. approach as well. The two roughly sp^3 hybrid orbitals of the two borons and the 1*s* orbital of one hydrogen will generate three M.O.'s: one *bonding*, one *non-bonding* and one *antibonding* as shown in Fig. 13.4. The two electrons will obviously stay as paired spins in the bonding M.O. The same will be the case for the other (B H B) part i.e. the second paired spin will fill up the second bonding M.O. The diamagnetism of B_2H_6 will thus have a reasonable explanation. In some reactions of diborane the bridging BH_2B framework remains unaltered. Thus B_2H_6 reacts with $B(CH_3)_3$ to give products like $B_2H_5CH_3$, $B_2H_4(CH_3)_2$, $B_2H_3(CH_3)_3$ and $B_2H_2(CH_3)_4$ but no product beyond $B_2H_2(CH_3)_4$. Thus only the terminal atoms are replaced by CH_3 groups.

Fig. 13.5 depicts the structure of tetraborane B_4H_{10}.

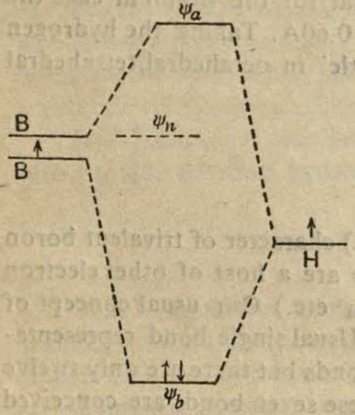

FIG. 13.4. M.O. description of one (B H B) banana bond.

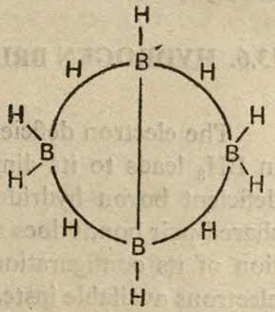

FIG. 13.5. B_4H_{10}

Hydrogen Bond and Hydrogen Bridge Bond: For a hydrogen bond to be operative in HF, H_2O, NH_3 the binary hydride must be polar. Polarity can arise only when the hydride forming element (eg: F, O, N) differs widely in its electronegativity from hydrogen. This results in accumulation of residual positive charge on hydrogen and residual negative charge on the other element. Electrostatic interaction between dipolar ends then leads to association. On the contrary in hydrogen bridge bond boron and hydrogen have similar electronegativities, namely 2.0 and 2.1. No polarity and hence no association can occur. Hydrogen bridge bonds are forced by electron deficiency of the compounds.

13.7. ISOLATION OF HYDROGEN

Methods of commercial production of hydrogen must start with raw materials of low cost and great abundance. Such materials are water, coke and hydrocarbon gases.

In the Bosch process, a mixture of hydrogen and carbon monoxide called water-gas is produced by the reaction of steam and hot coke:

$$C + H_2O \xrightarrow[1000°C]{heat} H_2 + CO$$

The reaction being endothermic the coke has to be kept hot and this is done by blowing air through when the exothermic reaction between carbon and oxygen takes place.

$$C + O_2 \longrightarrow CO_2 + heat$$

The CO_2 and air are allowed to escape. The endothermic and exothermic reactions are alternated to give intermittent production of H_2 and CO. The water gas is then mixed with excess steam and is allowed to react over a heated bed of Fe_2O_3 and Cr_2O_3:

$$(H_2 + CO) + H_2O \xrightarrow[500°C]{catalyst} H_2 + H_2 + CO_2$$

This above reaction is known as *water gas shift reaction*. The CO_2 is absorbed in cold water under pressure. This may also be absorbed at ~70°C by aqueous ethanolamine which forms ethanolamine carbonate:

$$2HO.CH_2.CH_2.NH_2 + H_2O + CO_2 \underset{\sim 120°C}{\overset{\sim 70°C}{\rightleftarrows}} (HO.CH_2.CH_2.NH_3)_2CO_3$$

The above Bosch process may be little modified by changing from coke to hydrocarbons. Enough hydrocarbons are rejected in the 'cracking' of crude petroleum. The hydrocarbon and steam are allowed to react at ~800°C over a nickel catalyst:

$$CH_4 + H_2O \rightarrow 3H_2 + CO$$
$$C_3H_6 + 3H_2O \rightarrow 3CO + 6H_2$$

The issuing gas is mixed with more steam at a lower temperature (~500°C), which converts CO to CO_2. The dioxide is then taken care of as described above.

Hydrogen is also obtained as a by-product of industrial scale electrolysis of aqueous sodium chloride. Chlorine gas is liberated at the anode and hydrogen at the cathode. The liberation of H_2 at the cathode makes the cathode solution alkaline due to hydroxide ion.

Very pure Hydrogen: Very pure hydrogen may be obtained by electrolysis of barium hydroxide solution in U-shaped tubes fitted with nickel electrodes The hydrogen liberated at the cathode is led through a hot platinum gauze

at the cathode: $2H^+ + 2e \rightarrow H_2$

at the anode: $2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e$

(to remove any oxygen: $2H_2 + O_2 \rightarrow 2H_2O$) and is then dried by solid KOH and P_4O_{10}. The gas may contain at this stage little nitrogen. It is now led into an evacuated bulb containing hot palladium. Palladium readily absorbs hydrogen (approximate formula PdH). The nitrogen is then pumped off and the palladium is heated strongly when pure hydrogen is given out.

It is interesting to note that if water is electrolysed with palladium electrodes no evolution of hydrogen takes place at the cathode for sometime—evidently due to adsorption of the hydrogen by the palladium cathode. Furthermore if these palladium electrodes are interchanged, then for sometime no evolution is observed even at the anode—because the released oxygen reacts with the hydrogen absorbed earlier by the palladium cathode.

13.8. USES OF HYDROGEN

Some of the important uses of hydrogen are given below:

1. Hydrogen is used in the manufacture of a number of industrially important compounds: ammonia ($N_2 + 3H_2 \rightarrow 2NH_3$, methanol ($2H_2 + CO \rightarrow CH_3OH$; catalytic hydrogenation), formaldehyde ($2CH_3OH + O_2 \rightarrow 2HCHO + 2H_2O$; silver gauze catalyst, 500—600°C).

2. Catalytic hydrogenation of liquid vegetable oils (coconut oil, cotton seed oil) to solid fats is accomplished by hydrogenation at $\sim 175°C$ in the presence of finely divided nickel catalyst. The solid fats are used in the manufacture of soaps, candles or marketed as margarines, vegetable shortenings etc.

3. Atomic hydrogen torch capable of giving an exceedingly high temperature ($> 3000°C$) is very useful in welding jobs since the hydrogen maintains a reducing atmosphere around the metal pieces to be welded, and thus prevents their oxidation which otherwise results in poor welding.

4. This is also a suitable reducing agent for metal oxides.

5. Deuterium oxide (heavy water) is used as a moderator in nuclear reactors since it is very effective in reducing the energies of the fast neutrons. Thus virulence of a nuclear reaction is controlled. Heavy water is also used in deuterium exchange studies.

13.9. ANALYTICAL REACTIONS OF HYDROGEN

Hydrogen gas combines with oxygen to form water. Hydrogen, when present in a mixture of gases, may be separated by absorption on spongy palladium. The gas may be released from palladium by heating and detected by its reactions with oxygen.

For quantitative estimation of hydrogen present in a compound a weighed amount of the latter is heated in oxygen atmosphere and in presence of copper (II) oxide. The water vapour formed is absorbed by a suitable dehydrating agent such as concentrated H_2SO_4, P_4O_{10} or anhydrous magnesium perchlorate and weighed. During such combustion organic compounds also produce CO_2 which is absorbed in sodalime tubes and weighed, after the water vapour has been absorbed suitably.

STUDY QUESTIONS

1. Hydrogen can be included both in group IA above the alkali metals and in group VIIB above the halogens. Discuss.

2. What are isotopes? How are the isotopes of an element expected to behave? Compare the behaviours of protium and deuterium.

3. H_2S has a higher molecular weight than H_2O and yet it is a gas at room temperature whereas H_2O is a liquid. Comment.

4. A proton is always solvated. Why?

5. Zinc has a standard potential −0.763 volts but it does not readily liberate hydrogen from water. Furthermore pure zinc reacts very reluctantly with aqueous acid. Explain (consult Chapter 30).

6. BH_3 readily polymerises but CH_4 does not. Again NH_3 and H_2O are substantially associated. Explain these differences on the basis of the electronic configurations of B, C, N and O.

7. Using ionisation potential, electronegativity and Fajans' rules proceed to predict the chemical behaviour of an element with the electronic configuration, $1s^1$.

8. How do you propose to obtain heavy water, heavy hydrogen and heavy sulphuric acid? How would you expect the ionic mobilities of metal ions to vary in ordinary water and heavy water?

9. Discuss the different ways hydrogen can enter into chemical combinations.

10. Give an outline of the industrial preparation and uses of hydrogen.

11. Deuterium is an isotope of hydrogen but not an allotropic modification. Comment

12. Write short accounts of *(a)* ortho and para hydrogen *(b)* atomic hydrogen.

13. Give a classification of binary hydrides and their distinguishing features. Discuss how the ionisation potential and electronegativity of the parent element decide the bond type of the hydride.

14. Anhydrous HCl is a bad conductor of electricity but aqueous HCl is an excellent conductor. Comment.

15. Hydrogen can exhibit both positive and negative behaviour in its compounds. Discuss

16. Compare and contrast hydrogen bond and hydrogen bridge bond.

17. Cite some reactions where hydrogen participates as an oxidant. What properties substantiate such unusual character of hydrogen?

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14

Group IA. The Alkali Metals

The alkali metals are distributed very widely in the earth's crust. The percent abundances by weight are: Li(0.006%); Na(2.5%); K(2.4%); Rb(0.03%); Cs (0.0007%). With increase in atomic number the elements become rare. Lithium occurs in small amount because of its disappearance through natural processes of nuclear bombardment.

14.1. COMPARATIVE STUDY OF THE ALKALI METALS

14.1.1. General Considerations: The six elements lithium, sodium, potassium, rubidium, caesium and francium constitute the family of the alkali metals. This is a most coherent group in the Periodic Table. Their properties are very consistent with their electronic configurations (Table 14.1).

Table 14.1. Electronic Configurations and Some Properties of Groups IA Elements

Element	Atomic Number	Electronic Configuration	Ionisation Potential (*ev*)	Electronegativity
Li	3	[He] $2s^1$	5.39	1.0
Na	11	[Ne] $3s^1$	5.14	0.9
K	19	[Ar] $4s^1$	4.34	0.8
Rb	37	[Kr] $5s^1$	4.18	0.8
Cs	55	[Xe] $6s^1$	3.89	0.7
Fr	87	[Rn] $7s^1$		0.7

The alkali metals have one electron in an *s* orbital over a noble gas core. Their low first ionisation potentials reflect the ease with which they assume noble gas configurations. With increasing atomic number the *s* electron is farther and farther from the positive nucleus. This leads to a steady decrease in their ionisation potentials. The alkalies have the largest size among the elements of each period. Large size and small charge of the cations, according to Fajans, favour formation of ionic compounds (Chapter 5). This tendency of forming ionic compounds increases down the group. The electron affinities and the electronegativities of the alkalies are also small. When the alkalies combine with other elements there results a wide difference in electronegativities, which leads to the formation of ionic compounds. Summing up it may be stated that *the chemistry of the alkalies is the chemistry of their ions.*

Note that there is no scope for the alkalies to exhibit an oxidation state +2 since that would mean utilising electrons from the very stable noble gas configuration—a difficult proposition indeed. In fact the second ionisation potentials are prohibitively large:

Element	Ne	Na	Na^+	Ar	K	K^+
I.P. (*ev*)	21.56	5.14	47.29	15.75	4.34	31.81

The ease with which the valence electrons are lost is also reflected in their standard electrode potentials ($M^+ + e \rightleftharpoons M; E^\circ$) being the most negative of all metals. The E° values become more negative from sodium to caesium (Table 14.2). These data mark the alkalies as the most vigorous reducing agents known. Their ions consequently are the most difficultly reducible ones.

As expected from their electronic configurations, their atomic radii and ionic radii increase systematically with atomic number from lithium to caesium. The melting points, boiling points and hardness decrease with increasing atomic number, indicating a weakening in the bonding between the atoms. The atoms are partly associated as diatomic molecules and the dissociation energies of the molecules decrease from 26.3 K cal/mole for Li_2 to 10.4 Kcal/mole for Cs_2. Compared to other metals, densities of the alkalies are low because of their large size. Note that with increasing atomic number the densities also increase.

Table 14.2. Some More Properties of Group IA Elements

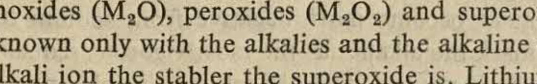
Element	Atomic Radius (A)	Ionic Radius M^+(A)	M.P. (°C)	B.P. (°C)	Density (g/ml)	E°(volts) $M^+ + e \rightleftharpoons M$
Li	1.52	0.60	174	1317	0.534	−3.04
Na	1.86	0.95	97.9	883	0.97	−2.71
K	2.31	1.33	63.7	760	0.87	−2.92
Rb	2.44	1.48	38.5	668	1.53	−2.99
Cs	2.62	1.69	28.5	705	1.87	−3.02

14.1.2. Chemical Behaviour: Obeying Fajans' rules nearly all their chemical compounds are ionic in nature. The remarkable ability of the alkalies to stabilise ionic compounds is shown by the existence of otherwise unstable anions such as bicarbonates, bisulphites, superoxides and the polyhalides as crystalline alkali metal salts. The lithium ion having the smallest size in this series, sometimes gives rise to some covalent tendency. Taking complex formation as a manifestation of covalence it appears that lithium and to a smaller extent sodium may form some covalent compounds.

Hydrides: Alkali metal hydrides are all ionic in nature. They are formed by the direct combination of hydrogen and the alkalies at 350—600°C. They are all colourless, crystalline solids with reasonably high melting points. Their crystal structures are of the ionic type (NaCl structure). On electrolysis of the fused hydrides alkali metals as usual migrate to the cathode but hydrogen is liberated at the anode. This behaviour shows that in the alkali metal hydrides hydrogen is present as the hydride anion. This negative character has been imposed on hydrogen by the extreme electropositive nature of the alkalies.

$$MH \xrightarrow{\text{fused}} M^+ + H^- \xrightarrow{\text{electrolysis}} \begin{cases} \text{at the cathode} : & M^+ + e \rightarrow M \\ \text{at the anode} : & H^- \rightarrow H + e \\ & 2H \rightarrow H_2 \end{cases}$$

Oxides: The alkalies readily react with oxygen, forming a number of binary compounds: monoxides (M_2O), peroxides (M_2O_2) and superoxides (MO_2). The superoxides are known only with the alkalies and the alkaline earths. The larger the size of the alkali ion the stabler the superoxide is. Lithium forms only the monoxide, sodium upto peroxide and the other alkalies upto the superoxide. Crystal structure determination shows ionic type (NaCl) lattice. Lithium and sodium ions are too small to fit into the holes created by the packing of the big superoxide anions and hence only the bigger alkali ions can form a stable lattice (Chapter 6). Insertion of bigger cations minimises 'rattling'. Peroxides and superoxides are highly hydrated eg: $Na_2O_2.8H_2O.CaO_2.8H_2O$. Alkali metal peroxides are powerful oxidants. They oxidise chromium (III) to chromate (VI) and manganese (II) to manganate (VI). The superoxide ion has one unpaired electron whose existence is shown by the paramagnetism of the salts ($\mu \sim 1.9$ B.M. corresponding to one unpaired electron). On valence-bond model we have the following two resonating structures (I and II), which are often expressed as a three-electron bond structure (III). On the molecular orbital theory we have to put one more electron in the antibonding π^* molecular orbital of the O_2 molecule (Fig. 5.8, Chapter 5). This would reduce the number of unpaired electrons from 2 in O_2 to 1 in O_2^-.



I II III

The oxides are all readily hydrolysed by water to give the metal hydroxides. Since the alkali metals have high negative standard potentials they react readily with water to form hydroxides with evolution of hydrogen.

$$M_2O + H_2O \rightarrow 2M^+ + 2OH^-; \; M_2O_2 + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2O_2$$
$$2MO_2 + 2H_2O \rightarrow O_2 + 2M^+ + 2OH^- + H_2O_2$$

Halides: Alkali metal halides are easily obtained by the direct combination of the elements. They are typical ionic compounds with high melting and boiling points, ionic crystal structure and high conductivity in the fused state. The radius ratio (M^+/X^-) rule predicts coordination number four for lithium chloride, six for sodium chloride and potassium chloride, and eight for rubidium chloride and caesium chloride. Contrary to prediction lithium chloride has a coordination number six, this being due to more favourable lattice energy.

Nature of the aqueous ions: The alkali salts, being typical ionic compounds, readily dissolve in water which is an ionising solvent of high dielectric constant. The aqua ions are thus produced. The lithium ion, being the smallest in size, would be expected to move fastest in solution but experiments identify lithium ion as the slowest moving of the alkalies. On the other hand the biggest sized caesium ion is the fastest moving (Table 14.3). Hydration involves coordination of aqua molecules both in the inner sphere and in the outer sphere. Interestingly the hydration energy (energy released when one gm. mole of an ion in the gaseous state is dissolved in water) falls from lithium to caesium, once again pointing to the greater complexing ability of lithium ion. Because of the lowest ionic mobility, lithium ion also transports the least current through a solution. Its transport number (= fraction of the total current carried) is thus the lowest in the series. That the size of the aqua lithium ion is distinctly bigger than the other aqua alkali ions is shown by their hydrated radii (Table 14.3). In view of the decreasing order of the hydrated radii of the alkali ions ($Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$) the ease of binding of these hydrated ions on a cation exchange resin bed follows the reverse order $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. Because of the smallest hydrated radius Cs^+ will have the highest charge density and hence will be attracted most readily by the negative part of the resin.

Table 14.3. Hydration Energies and Ionic Mobilities of Group IA Elements

Property	Li	Na	K	Rb	Cs
Ionic Radius (A)	0.60	0.95	1.33	1.48	1.69
Hydrated Radius (A)	3.40	2.76	2.32	2.28	2.28
Hydration energy (Kcal/mole)	121	95	76	69	62
Ionic mobility $\times 10^5$ (cm/sec/volt)	33.5	43.5	64.2	67.2	68

Nature of the solution of the alkalies in liquid ammonia: In the presence of catalysts, e.g. iron, the alkali metals react with liquid ammonia to form metal amides and hydrogen: $M + NH_3 \rightarrow MNH_2 + \frac{1}{2}H_2$. In the absence of any impurity the alkalies dissolve in ammonia without hydrogen evolution and they can be recovered unchanged on evaporation of the solvent. This dissolution gives ammoniated cations and ammoniated electrons:

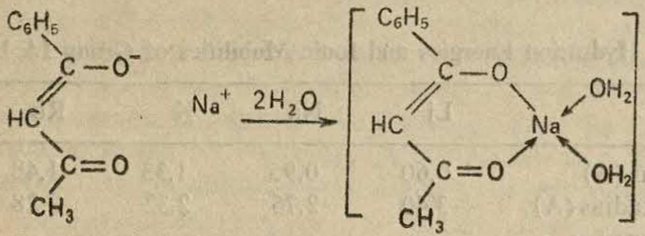
$$Na \rightarrow Na^+ + e; \quad Na^+ + 4NH_3 \rightleftharpoons [Na(NH_3)_4]^+; \quad e + xNH_3 \rightleftharpoons [e(NH_3)_x]^-$$

The transport and conductance behaviour indicate that the mobility of the anion is almost as great as ~280 times that of the cation. Thus the anion is believed to be more or less a solvated electron. The solutions of lithium, sodium, potassium, etc give identical blue colour. The blue colour is due to a long tail of an absorption band occurring in the infrared (~15000A). The tail absorbs in the red region of the spectrum so that the solution looks blue in transmitted light. The transition is a very unusual type ($1s \rightarrow 2p$). Because of the solvated electron, these solutions are very strong reducing agents.

Complex compounds: The tendency to complexation decreases with increasing atomic number. The overall tendency, however, is much less than what we find in the multivalent transition metals.

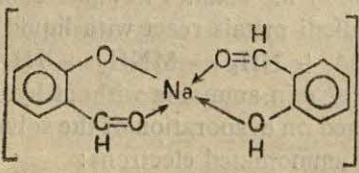
Hydration of the alkali ions is a revelation of their tendency to complexation. As expected lithium ion is the most hydrated. Of all the alkalies, lithium forms the widest series of organoalkali compounds. Organolithium compounds resemble well-known Grignard reagents. These are obtained by the interaction of lithium metal and alkyl/aryl halides in benzene or petroleum ether. Organolithium compounds are low-melting solids and are soluble in non-polar solvents. These are properties of typical covalent compounds.

A few non-ionic complex compounds with organic bidentate ligands have been described. Sodium ethylate reacts with benzoylacetone to form the salt sodium benzoylacetonate. This compound is ionic (Na^+ ion) and is insoluble in non-polar solvents such as benzene or toluene. On recrystallisation from rectified spirit the compound takes up two molecules of water, turns into a non-electrolyte and now shows perceptible solubility in benzene. It is obvious that sodium has now attained a coordination number four and a complex (14-I) has been formed:



(14-I)

Coordination of the two water molecules has added to the stability of the complex presumably through the attainment of a suitable coordination number and a noble gas configuration. A complex of sodium with salicylaldehyde has also been obtained (14-II).



(14-II)

Quite recently several other ligands, namely 8-hydroxy-quinoline (HL), o-aminobenzoic acid, nitrosonaphthols have been reported to give complexes with several alkali metals. Taking 8-hydroxyquinoline as an example, the complexes are of the type $[ML(HL)]^0$ (M = Li, Na) or $[ML(HL)_2]$ (M = K, Rb, Cs). Some of these complexes, however, show significant dissociation in polar non-aqueous solvent—an indication that alkali metals do not form stable complexes.

It may be recalled (Chapter 8) that alkali metals are generally regarded as 'class a' metals (hard acids) and so would be expected to complex, if at all, with hard donor ligands (hard bases), that is, with ligands containing nitrogen or oxygen as donor atoms. The complexes reported so far are of the hard acid-hard base combination.

Over the last few years several remarkable macrocyclic polyethers (often called *crown ethers*) have been synthesised. Several poly macrocyclic ethers with nitrogen bridge heads (often called *cryptands*) can readily trap alkali or alkaline earth metal ions of suitable size inside the *hole* of the ligand. Such a cryptand is $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N(= L)$. It forms a complex with rubidium thiocyanate having the composition $[Rb(L)]SCN.H_2O$.

14.2. PECULIARITIES OF LITHIUM: DIAGONAL RELATIONSHIP WITH MAGNESIUM

In Chapter 5 we have discussed the basis of the diagonal relationship observed in the Periodic Table among pairs of elements that belong to different groups and periods. One such pair comprises lithium and magnesium. The two elements are of similar deforming power and have close charge/radius ratios:

Element	Li	Mg
Charge on the ion	+1	+2
Ionic Radius (A)	0.60	0.65
Charge/radius	1.60	3.08

Although lithium is a member of the family of the alkalies and although it shows many properties typical of the alkalies, there are properties where lithium shows difference from the other alkalies. In these points of differences lithium resembles magnesium of group IIA. The small size and consequent deforming power make lithium somewhat different from the other alkalies.

The reactivity of the alkali metals towards chemical reagents increase in general from lithium to caesium. Lithium is slow to react with water, sodium reacts more vigorously, potassium so vigorously that the liberated hydrogen burns, and rubidium and caesium explode. However with nitrogen it is lithium alone that forms an ionic lithium nitride Li_3N. Magnesium too forms an ionic nitride Mg_3N_2. Both lithium and magnesium are used to remove nitrogen from other gases.

The ease of forming peroxides and superoxides generally increases with increasing atomic number. Lithium forms only the monoxide, sodium upto per-

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oxide, and potassium, rubidium and caesium upto superoxides. The small Li^+ ion cannot sufficiently stabilise the larger anions O_2^{2-} or O_2^-.

LiOH decomposes on heating to Li_2O whereas the other alkali hydroxides sublime unchanged. In this respect, lithium is similar to magnesium whose hydroxide also changes to oxide. Lithium hydroxide is considerably less soluble in water than the other alkali hydroxides. Magnesium hydroxide is also sparingly soluble in water.

Of the alkali carbonates the lithium compound is thermally the least stable and decomposes to Li_2O and CO_2. Magnesium carbonate also is thermally unstable and breaks up into MgO and CO_2.

Double sulphates of the alum type $M^I M^{III}(SO_4)_2 . 12H_2O$ can be made with all the alkali metals except lithium (M^I = Na, K, Rb, Cs, NH_4; M^{III} = Al, Cr, Fe, Mn, Co, Ti, V, Rh, Ir). Not all these M^{III} ions will combine with all the M^I ions. Formation of alums seems to depend on the size of ions. Both the cations are surrounded by a group of six water molecules. The lithium ion evidently is too small in size to accommodate six water molecules. In fact for none of the elements in the lithium period is it possible to have more than four lone pairs of electrons around the element.

Solubilities of certain lithium compounds differ very widely from those of the other alkalies, and in these respects lithium again resembles magnesium. The solubilities of all the alkali halides in water are high. Lithium fluoride is the only exception, it being sapringly soluble. Magnesium fluoride is also sparingly soluble. The solubilities of the alkali perchlorates sharply fall off from sodium to caesium. Lithium perchlorate again is an exception being extremely soluble. So also is magnesium perchlorate which is a celebrated dehydrating agent. Unlike the other alkali carbonates and phosphates but like the corresponding magnesium salts, lithium carbonate and phosphate are sparingly soluble in water.

Several lithium compounds are of chemical importance. Lithium alkyls are used in organic syntheses where they bring about reactions similar to those of Grignard reagents, RMgX. $LiAlH_4$ and $LiBH_4$ are used extensively as reducing agents in organic syntheses, the compounds being soluble in organic solvents (Chapter 16).

14.3. FRANCIUM

This element, the last member of the alkali family, was for long a missing element of the Periodic Table. It is found as a product of the decay of actinium-227. Actinium-227 was primarily known as a beta emitter but a feeble alpha radiation also accompanied the beta rays. The alpha emission was earlier thought to be arising from some impurity in the actinium. Percy finally proved that simultaneous emission of alpha rays was real and that this alpha emission produced francium-223. This isotope is a beta emitter (half life, 21 min.) and decays to radium-223. Enough tracer work has been done with francium to confirm that it belongs to group IA and that it resembles the chemistry of the alkalies in general.

$$ {}^{227}_{89}\mathrm{Ac} \begin{cases} \xrightarrow{99\%} {}^{227}_{90}\mathrm{Th} + {}^{0}_{-1}e \\ \xrightarrow[1\%]{} {}^{223}_{87}\mathrm{Fr} + {}^{4}_{2}\mathrm{He} \end{cases} $$

$$ {}^{223}_{87}\mathrm{Fr} \longrightarrow {}^{223}_{88}\mathrm{Ra} + {}^{0}_{-1}e $$

Francium is the most electropositive element. Coprecipitation studies have revealed marked similarities between caesium and francium. Francium is carried down completely on crystals of Cs_2PtCl_6, Cs_2SnCl_6 and $Cs_2[Co(NO_2)_6]$ as the respective salts. Francium can be precipitated from HCl solution by silicotungstic acid.

14.4. COMPOUNDS OF THE ALKALI METALS

14.4.1. Sodium Phosphates: Phosphoric acid is a weak tribasic acid. The normal and the two acid phosphates are obtained under different reaction conditions.

Disodium hydrogen phosphate, Na_2HPO_4, is obtained by neutralising phosphoric acid with NaOH in presence of phenolphthalein and evaporating the solution to obtain crystals of the heptahydrate, $Na_2HPO_4.7H_2O$.

Sodium dihydrogen phosphate is prepared by adding phosphoric acid to the disodium salt until a little of the solution no longer precipitates barium ion. The solution is then concentrated and crystallised.

Trisodium phosphate is produced by the interaction of disodium hydrogen phosphate and sodium hydroxide in hot water, being followed by concentration and crystallisation.

Sodium ammonium hydrogen phosphate, $NaNH_4PO_4.4H_2O$, also called *microcosmic salt* is made by preparing a concentrated solution of the disodium salt and NH_4Cl in 1:1 ratio in hot water. Sodium chloride is removed and the filtrate allowed to crystallise. 'Microcosmic salt decomposes on heating to give *sodium metaphosphate:*

$$NaNH_4HPO_4 \rightarrow NaPO_3 + NH_3 + H_2O$$

Sodium metaphosphate is really *hexametaphosphate*, $(NaPO_3)_6$. It is used under the trade name *calgon** for softening water, calcium and magnesium ions being inactivated by way of complexation:

$$Na_2[Na_4(PO_3)_6] + CaSO_4 \rightarrow Na_2[Na_2Ca(PO_3)_6] + Na_2SO_4.$$

For further details see Chapters 15 and 18.

14.4.2. Sodium Carbonate: This is obtained commercially by Solvay process. Carbon dioxide is led into a concentrated solution of sodium chloride and ammonia, when ammonium carbonate and then ammonium bicarbonate are formed. This latter reacts with sodium chloride to give sodium bicarbonate via metathesis. The sodium bicarbonate is then heated to get sodium carbonate. The carbon dioxide is recirculated.

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*'Calgon' meaning 'Calcium gone'.

$$2NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2CO_3$$
$$(NH_4)_2CO_3 + H_2O + CO_2 \rightarrow 2NH_4HCO_3$$
$$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$$
$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

Electrolysis of brine (section 14.4.3) can be manipulated to give NaOH. A mixture of CO_2 and steam is introduced into the compartment where NaOH is being formed. By adjusting the input of CO_2 either bicarbonate or the carbonate is produced:

$$CO_2 + NaOH \rightarrow NaHCO_2 \ ; \ 2NaOH + CO_2 \rightarrow Na_2CO_2 + H_2O$$

If electricity is cheap this process is excellent as there are no waste products. Anhydrous Na_2CO_3 is known as *soda ash* and the decahydrate as *washing soda.*

Carbonic acid is a weak acid and therefore soluble alkali metal carbonates and bicarbonates are hydrolysed to produce basic solution:

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^- \ ; \quad HCO_3^- + H_2O \rightarrow H_2CO_3 + OH^-$$

Thus neutralisation of sodium carbonate by an acid goes in two steps: the first step attains a pH ~8.5 and the second step a pH ~4. It is therefore obvious that neutralisation 'end point' during titration of a sodium carbonate solution by an acid will depend on which of the above steps is made use of. Thus, phenolphthalein, which changes colour at pH ~8.5, will give a titre value that will be half of the titre value shown by methyl orange changing colour at pH ~4. These titrations form the basis of estimation of carbonate and bicarbonate present in a mixture. A known volume of the mixture is first titrated with a standard acid solution using phenolphthalein or better thymol blue-cresol red mixed indicator (colour change: violet to blue at pH ~8.4). The volume (M ml) of the acid (say HCl) corresponds to half the carbonate present. Another equal aliquot is then titrated with methyl orange. This second acid volume (m ml) gives the total amount of the bicarbonate plus the total carbonate. Thus $2M$ corresponds to the carbonate and $m-2M$ corresponds to the bicarbonate.

Sodium carbonate finds application in glass industry. Soft or soda lime glass is made by fusing a mixture of $CaCO_3$, Na_2CO_3 and SiO_2. It is also used in paper industry, textile manufacture etc. Sodium bicarbonate is used in baking powder. Some harmless acidic substance (potassium hydrogen tartrate) is present in the baking powder alongwith $NaHCO_3$. Thus on heating the cake dough with baking powder CO_2 is released, which makes the dough swell and imparts a fluffiness to the cake.

14.4.3. Sodium Hydroxide: This is produced commercially by electrolysis of a sodium chloride solution using a mercury cathode and carbon anodes.

Sodium is discharged on mercury and forms an amalgam. This amalgam is treated with water to produce sodium hydroxide. The process is accomplished in three chambered electrolysis cell with slate partitions reaching almost to the bottom. The cell has a thick layer of mercury on the floor. The side compartments carry the carbon anodes and the mercury serves as the cathode. The central compartment carries water and the other two a strong brine solution. On electrolysis chlorine is given off at the anode chambers, which is then made to move into the middle compartment by a shaking device, where the amalgam reacts with water to form sodium hydroxide.

An inspection of standard electrode potentials convinces us that it is more difficult to reduce Na^+ ion than H^+ ion. On electrolysis of a neutral brine solution we would expect release of H_2 at the cathode instead of deposition of sodium.

$$Na^+ + e \rightleftharpoons Na; \qquad E^\circ = -2.71 \text{ volts}$$

$$2H^+(1.0 \times 10^{-7} M) + 2e \rightleftharpoons H_2; \qquad E^\circ = -0.41 \text{ volts}$$

$$O_2 + 2H_2O + 4e \rightleftharpoons 4OH^-(1.0 \times 10^{-7}M); \qquad E^\circ = +0.82 \text{ volts}$$

$$Cl_2 + 2e \rightleftharpoons 2Cl^-; \qquad E^\circ = +1.36 \text{ volts}$$

But proton transfer from water to a mercury surface needs a high activation energy. *Mercury has a high hydrogen overvoltage while sodium has a very low overvoltage on mercury*. So on electrolysis sodium is discharged on mercury in preference to hydrogen. The resulting amalgam is then reacted with water in the middle compartment of the cell to form sodium hydroxide (and H_2). It also follows from the above standard potentials that OH^- ion is a stronger reducing agent than Cl^- ion so that it will be easier to oxidise OH^- ion to O_2 at the anode than Cl^- to Cl_2. Once again our prediction goes wrong. At the anode chlorine is evolved in preference to oxygen. *Oxygen has a high overvoltage on mercury.*

The reader should note that had we used an open cell then the anode product and the cathode product would have interacted, in the cold, to give NaOCl and, in the hot, $NaClO_3$ (Chapter 20).

Carbonate-free NaOH solution is made by boiling distilled water to remove CO_2 and allowing to cool in a flask fitted with a sodalime guard tube. 3-4 cm deep ether layer is added being followed by pieces of clean sodium. Sodium and sodium hydroxide cannot come in contact with atmospheric CO_2. The ether is removed with a pipette and finally by heating.

It is a white hygroscopic solid. Large quantity is used in the manufacture of soap via reaction with fats. NaOH is used in textile industry for mercerizing cotton thread by dissolving out undesirable fuzzy fibres. It is also used in rayon making, in the purification of petroleum, in the manufacture of paper etc.

14.4.4. Sodium Cyanide: Sodium is heated (~700°C) in covered pots into which gaseous ammonia is introduced. From time to time small amounts of charcoal is added. First sodamide is formed, which reacts with carbon to form sodium cyanamide, which then reacts with more carbon to give sodium cyanide.

$$2NH_3 + 2Na \rightarrow 2NaNH_2 + H_2$$

$$2NaNH_2 + C \rightarrow Na_2NCN + 2H_2$$

$$Na_2NCN + C \rightarrow 2NaCN$$

Large quantities of sodium cyanide are used in electroplating and in the extraction of silver and gold.

14.4.5. Sodium Peroxide: It is prepared in bulk scale by the action of purified air over sodium maintained at 300°C in iron pipes. The crude Na_2O_2 is dissolved in ice water to form a concentrated solution, which is then treated with alcohol to crystallise the octahydrate, $Na_2O_2.8H_2O$. It is yellow but becomes white on exposure to moist air due to the formation of NaOH and Na_2CO_3. An aqueous solution is alkaline due to hydrolysis. On heating an aqueous solution oxygen is evolved:

$$Na_2O_2 + 2H_2O \rightarrow 2NaOH + H_2O + \tfrac{1}{2}O_2$$

It is a strong oxidant:

$$Cr_2O_3 + 3Na_2O_2 \rightarrow 2Na_2CrO_4 + Na_2O$$
$$MnO_2 + Na_2O_2 \rightarrow Na_2MnO_4$$
$$2FeCr_2O_4 + 7Na_2O_2 \rightarrow Fe_2O_3 + 4Na_2CrO_4 + 3Na_2O$$
$$2FeS_2 + 15Na_2O_2 \rightarrow Fe_2O_3 + 4Na_2SO_4 + 11Na_2O$$

It oxidises ammonia to nitrogen, oxides of nitrogen to nitrates and sulphides to sulphates. *It readily attacks filter paper so that for all laboratory work Na_2O_2 should be handled in glass wares.*

14.4.6. Sodium Sulphate: This is obtained as a by-product during the manufacture of HCl from NaCl. Common salt is taken in a thick iron pan which is kept hot. Sufficient H_2SO_4 is added when the reaction: $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$ occurs. The mixture of NaCl and $NaHSO_4$ is then transferred to a muffle furnace when at ~ 500°C further reaction occurs: $NaHSO_4 + NaCl \rightarrow Na_2SO_4 + HCl$. The decahydrate is called Glauber's salt. It is used in glass industry.

14.4.7. Sodium Sulphite and Bisulphite: Sodium sulphite is made by treating NaOH solution with SO_2 to a neutral reaction:

$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$$

The bisulphite is prepared by saturating the above solution with SO_2:

$$Na_2SO_3 + SO_2 + H_2O \rightarrow 2NaHSO_3$$

Aqueous Na_2CO_3 may also be saturated with SO_2:

$$Na_2CO_3 + 2SO_2 + H_2O \rightarrow 2NaHSO_3 + CO_2$$

14.4.8. Sodium Sulphite: Sodium hydrosulphide, NaSH, is made by saturating an alcoholic solution of sodium with H_2S and precipitating NaSH by the addition of ether:

$$NaOC_2H_5 + H_2S \rightarrow NaSH + C_2H_5OH$$

The hydrosulphide decomposes to the sulphide on heating:

$$2NaSH \rightarrow Na_2S + H_2S$$

On a commercial scale Na_2S is made by reducing Na_2SO_4 with coal:

$$Na_2SO_4 + 4C \rightarrow Na_2S + 4CO$$

An aqueous solution of Na_2S is strongly alkaline due to hydrolysis.

14.4.9. Potassium Carbonate: The Solvay process cannot be applied in this case since potassium bicarbonate is too soluble to be precipitated by ammonium bicarbonate. To a cold concentrated solution of KCl is added hydrated magnesium carbonate and the suspension is treated with CO_2. Sparingly soluble potassium hydrogen magnesium carbonate separates. This is filtered and heated with water when magnesium carbonate precipitates out and CO_2 is evolved. The CO_2 and the magnesium carbonate are reused in the cycle. The filtrate is concentrated and potassium carbonate recovered.

$$MgCO_3.3H_2O + CO_2 \rightarrow Mg(HCO_3)_2 + 2H_2O$$

$$2KCl + Mg(HCO_3)_2 \rightarrow 2KHCO_3 + MgCl_2$$

$$KHCO_3 + MgCO_3.3H_2O + H_2O \rightarrow KHCO_3.MgCO_3.4H_2O$$

$$2(KHCO_3.MgCO_3.4H_2O) \rightarrow K_2CO_3+3H_2O+2MgCO_3.3H_2O+CO_2$$

14.4.10. Potassium Cyanide: This is prepared by passing ammonia gas over a fused mixture of potassium carbonate and carbon:

$$K_2CO_3 + C + 2NH_3 \rightarrow 2KCN + 3H_2O$$

Both sodium and potassium cyanide can also be obtained by fusing the respective ferrocyanide with the corresponding metal. The fused mass is then extracted and cyanide separated from iron:

$$Na_4[Fe(CN)_6] + 2Na \rightarrow 6NaCN + Fe;\ K_4[Fe(CN)_6] + 2K \rightarrow 6KCN + Fe$$

14.4.11. Potassium Ferrocyanide: This is commercially made by heating nitrogenous animal refuse such as blood, horns, leather scraps, etc. with iron filings and potassium carbonate. The product is treated with water and the solution concentrated till lemon-yellow crystals separate. On a small scale this is obtained by adding slight excess of potassium cyanide to a solution of ferrous sulphate till the initial precipitate of $Fe(CN)_2$ just dissolves. The solution is then evaporated to crystallisation:

$$FeSO_4 + 2KCN \rightarrow Fe(CN)_2 + K_2SO_4$$

$$Fe(CN)_2 + 4KCN \rightarrow K_4[Fe(CN)_6]$$

It is used in qualitative and quantitative analysis.

14.4.12. Potassium Ferricyanide: Potassium ferrocyanide is oxidised to the ferricyanide by chlorine or potassium permanganate:

$$2K_4[Fe(CN)_6] + Cl_2 \rightarrow 2K_3[Fe(CN)_6] + 2KCl$$

$$KMnO_4 + 8HCl + 5K_4[Fe(CN)_6] \rightarrow 6KCl + MnCl_2 + 5K_3[Fe(CN_6] + 4H_2O$$

14.4.13. Potassium Thiocyanate: This is obtained by fusing a mixture of $K_4[Fe(CN)_6]$ and K_2CO_3 with sulphur or by fusing KCN and sulphur:

$$K_4[Fe(CN_6)] + 4S \rightarrow 4KSCN + Fe(CN)_2$$

$$KCN + S \rightarrow KSCN$$

The SCN-ion can function as an ambidentate ligand by linking itself to a metal ion via nitrogen (*isothiocyanato*) or via sulphur (*thiocyanato*). Hard acid ions (Co^{3+}, Cr^{3+}) prefer to form isothiocyanato complex while soft acid ions (Pd^{2+}, Pt^{2+}) prefer to give thiocyanato complexes. With Pd^{2+} two isomeric complexes are known: $[Pd(dipy)(SCN)_2]$ and $[Pd(dipy)(NCS)_2]$. In crystal field strength—SCN-is close to Cl-while —NCS-is close to H_2O (Chapter 10).

14.5. ISOLATION OF THE ALKALI METALS

The alkali metals being the most electropositive are never found in nature in the elementary state. Sodium and potassium are widely distributed in nature in the form of silicates, *Chile saltpetre* ($NaNO_3$), *borax* ($Na_2B_4O_7$. $10H_2O$) etc. However the largest and a most useful source is sea water.

Since these elements are the strongest reducing agents they cannot be reduced from their oxides by other elements. The only useful technique is electrolysis of a suitable compound—a hydroxide or a chloride in fused state. Metallic sodium is produced by the electrolysis of fused sodium hydroxide (Castner process) or of fused sodium chloride (Downs process).

14.5.1. Sodium and Potassium : In the Castner process a cylindrical iron vessel serves as the container of sodium hydroxide which is kept fused by ring burners. Into the centre of the vessel there is an iron rod serving as cathode. Around the cathode there is a circular sheet of nickel or iron metal serving as the anode. In between the anode and the cathode there is placed a wire gauze cage so that sodium liberated at the cathode area cannot drift away. The sodium is collected from this area with a wire gauze spoon that retains the soft sodium but leaves behind the fused alkali.

$$NaOH \xrightarrow{\text{fused}} Na + OH^- \xrightarrow{\text{electrolysis}} \left| \begin{array}{l} \xrightarrow{\text{at the cathode}} Na^+ + e \rightarrow Na \\ \\ \xrightarrow[\text{at the anode}]{} 2OH^- \rightarrow H_2O \\ \qquad\qquad\qquad + \tfrac{1}{2}O_2 + 2e \end{array} \right.$$

Most of the metallic sodium is today made by the Downs process. Sodium chloride melts at~800° but in practice other salts such as $CaCl_2$ are added to lower the melting point of the electrolyte. The electrolysis chamber is made of firebrick. The anode is a carbon cylinder protruding into the electrolysis chamber through the bottom. All around the anode is a circular ring of iron or copper serving as the cathode. The anode area is covered by a dome shaped sealing to lead away the liberated chlorine gas. The circular cathode chamber is also covered and is connected to a receiver outside the electrolysis chamber for collecting the metallic sodium.

at the cathode : $Na^+ + e \rightarrow Na$

$$\mathrm{NaCl} \xrightarrow{\text{fused}} \mathrm{Na^+ + Cl^-} \xrightarrow{\text{electrolysis}} \left| \begin{array}{l} \longrightarrow \\ \\ \longrightarrow \mathrm{Cl^-} \rightarrow \mathrm{Cl} + e \end{array} \right.$$

at the anode : $2Cl \rightarrow Cl_2$

Potassium: An important source of potassium is *carnallite* $KCl.MgCl_2.6H_2O$. The crude carnallite containing some sodium chloride and magnesium sulphate along with small amounts of rubidium and caesium chloride is powdered and extracted with a hot 20% $MgCl_2$ solution from a previous operation. Most of the sodium chloride and magnesium sulphate remain undissolved. On cooling the extract KCl crystallises out. On further concentration and cooling an impure crop of KCl crystallises. The potassium metal may be obtained by electrolysis of fused KCl.

14.5.2. Lithium: The chief sources of lithium are: *lepidolite*, $Li_3Al(SiO_3)_3$; *petalite*, $LiAl(Si_2O_5)_2$ and *spodumene*, $LiAl(SiO_3)_2$. The silicate is fused with barium carbonate and the product extracted with HCl. The filtrate from this operation contains chlorides of Li, Al, Ba and K whereas silica is removed as an insoluble residue. The solution is evaporated to dryness and the solid is extracted with alcohol when lithium chloride alone passes into the alcohol. Evaporation of the solvent will leave behind solid lithium chloride. The free metal may be obtained by the electrolysis of the fused chloride using carbon rod as the anode and an iron rod as the cathode.

14.5.3. Rubidium and Caesium: The mother liquor after the extraction of KCl from carnallite can be processed for rubidium and caesium. The mother liquor contains rubidium carnallite $RbCl.MgCl_2.6H_2O$ and caesium carnallite $CsCl.MgCl_2.6H_2O$. Aluminium ion and sulphate ions are added and the alkali metals fractionally crystallised as their alums. The residue from the lithium separation of lithium ores can also be worked out to obtain aluminium rubidium (caesium) alums. These alums may be heated with calcium carbonate and ammonium chloride to obtain the alkali carbonates. These carbonates may be converted to the chlorides by HCl.

Interestingly some of the higher alkalies may be obtained by the reduction of some of their compounds by less active metals:

$$2CsCl + Ca \rightarrow CaCl_2 + 2Cs$$
$$K_2CO_3 + 2Na \rightarrow Na_2CO_3 + 2K$$

These are unusual reactions and are not predicted by a consideration of the standard potentials. The apparent conflict is resolved when we appreciate the high volatility of the alkali metal concerned. Even though caesium is more active than calcium, the equilibrium is shifted to the right because caesium (B.P. 705°C) boils away at the temperature of the reduction (B.P. of calcium, 1440°C). Elemental rubidium and caesium can also be obtained by electrolysis of fused chlorides under an inert atmosphere.

14.6. USES OF THE ALKALI METALS

The *alkali metals* have been put to a variety of uses. Sodium-lead alloy is used in the manufacture of lead tetraethyl. Photoelectric cells are composed of caesium, aluminium and barium (or strontium). Liquid sodium is used as an efficient coolant in nuclear reactors. The alkali metals, their alkyls and amalgams find extensive use in synthetic reactions.

14.7. ANALYTICAL REACTIONS OF THE ALKALI ELEMENTS

In the alkali ions transitions are possible from filled noble gas shell to the next higher quantum shell, for example for rubidium $4p^6 \rightarrow 4p^5 5s^1$. These need much energy and such transitions are located deep into the ultraviolet region. Alkali metal salts on being held over a Bunsen flame mostly dissociate into M^+ and X^-ions which ions give no characteristic colour. But most alkali salts (e.g. NaCl) decompose to some extent into component atoms. These alkali atoms give coloured spectra. For example in the sodium atom transition of an electron from 3*s* to several higher energy states occurs and when the excited electron returns from such an excited 3*p* level to 3*s* ground level it emits the characteristic golden yellow colour. As the atomic number increases the energy gap between successive levels decrease so that 4*p* to 4*s* transition in potassium should occur at a lower energy. However the characteristic violet colour of potassium is really due to a transition from 5*p* to 4*s* (and not due to 4*p* to 4*s*) occurring at a higher energy than in sodium, being at the violet end of the spectrum. It should be noted that the 5*p* to 4*s* transition is just one of the several possible transitions. It is also interesting to note that the higher energy transition in potassium is less realisable in a Bunsen flame. Hence the violet flame is less intense. The violet flame is masked by the presence of sodium. However this can be viewed if the flame is observed through cobalt glass blue filter which is not transparent to the yellow sodium flame. Lithium, rubidium and caesium are best detected by spectroscopic techniques.

Most alkali salts being quite soluble in aqueous medium have only a few useful precipitation reactions. Precipitation reactions are known only with large anions, and the larger the alkali cation the more insoluble salts it forms. Sodium forms an insoluble precipitate with zinc (or magnesium) uranyl acetate: $NaZn(UO_2)_3(CH_3COO)_9.6H_2O$ in dilute acetic acid solution. Whereas $NaClO_4$ is highly soluble K, Rb, Cs perchlorates are rather insoluble and the latter alkalies can be estimated gravimetrically as perchlorates. Sodium cobaltinitrite $Na_3[Co(NO_2)_6]$ and sodium tetraphenyl boron $Na[B(C_6H_5)_4]$ give quantitative precipitates suitable for gravimetric estimation of K, Rb and Cs.

STUDY QUESTIONS

1. The electronic configurations of a family of elements are: $[He]2s^1$;$[Ne]3s^1$;$[Ar]4s^1$; $[Kr]5s^1$. Proceed to expose their physical and chemical behaviours.

2. Why are the second ionisation potentials of the alkali metals so much higher than the first? What information do you get from these high values?

3. 'The chemistry of the alkalies is primarily the chemistry of their ions.' Justify.

4. Why do the alkali metals show only a slight tendency to complex formation?

5. Compare the products obtained by the electrolysis of (*a*) fused NaCl (*b*) cold aqueous NaCl (*c*) hot aqueous NaCl. (Consult also Chapter 20).

6. With sodium chloride as one of the starting materials write equations to illustrate how you would obtain (*a*) sodium metal (*b*) sodium hydroxide (*c*) sodium amide (*d*) sodium nitrate and (*e*) sodium peroxide.

7. Predict the trend in physical properties of the excited alkali metals with the electronic configurations: $1s^2 5s^1$; $1s^2 2s^2 2p^6 5s^1$; $1s^2 2s^2 2p^6 3s^2 3p^6 5s^1$. Compare with the properties of the ground state.

8. Give an account of the alkali metal hydrides. What special behaviour of hydrogen is noted in these compounds?

9. Why the alkali metals are not found in the free state in nature? Give an outline of their isolation and important uses.

10. Explain the basis of diagonal relationship. Cite some properties which illustrate such a relationship between lithium and magnesium. How then do you justify the inclusion of lithium in group IA?

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15

Group IIA Beryllium, Magnesium and the Alkaline Earths

Beryllium, magnesium, calcium, strontium, barium and radium are members of group IIA. Their relative per cent abundances in the earth's crust are:

Be(0.006%); Mg(2.0%); Ca(3.4%); Sr(0.02%); Ba (0.04%).

As with the alkali group the first member beryllium is present in very small quantity. This is due to the transmutation of the beryllium atoms under natural bombardment by protons. Presence of considerable amount of helium in beryllium minerals lends support to this hypothesis. With increasing atomic number the abundance again falls.

Very early in the development of chemical sciences chemists were familiar with a group of substances such as lime, strontia and baryta which were alkaline in nature and were much resistant to thermal decomposition. The three elements calcium, strontium and barium are therefore collectively called as alkaline earths.

15.1. COMPARATIVE STUDY OF THE GROUP IIA ELEMENTS

15.1.1. General Considerations: All the elements possess an s^2 configuration (Table 15.1) over a noble gas core. This s^2 configuration has led to their inclusion in group II of the Periodic Table. The s^2 electrons are lost to give bipositive oxidation states. The first ionisation potentials are rather low but the second potentials are rather high. In keeping with general expectation the potential values gradually decrease with increasing atomic number. This is a pointer that the basic properties increase down the group. It might be argued that that the elements may show both the +1 and the +2 states since the two ionisation potentials vary rather widely. Overwhelming amount of experimental facts points to a consistent bipositive state in the group. There is only one or two minor reports which claim that electrolysis of acidulated water with beryllium or magnesium electrodes is not in conformity with Faraday's law. The amount of hydrogen liberated at the cathode and the amount of beryllium (or magnesium) dissolved at the anode points to the metals passing into solution not entirely as +2 ions but to some extent as +1 ion. A study of the following ionisation potentials will convince us that in no case a +3 state can be realised:

Element	Ca	Ca^+	Ca^{2+}	Ar
I.P. (*e.v.*)	6.11	11.87	51.21	15.75

Table 15.1. Electronic Configurations and some Properties of Group IIA Elements

Element	Atomic Number	Electronic Configuration	Ionisation Potential (*e.v.*)	Electro-negativity
Be	4	$[He]2s^2$	9.32, 18.20	1.5
Mg	12	$[Ne]3s^2$	7.64, 15.03	1.2
Ca	20	$[Ar]4s^2$	6.11, 11.67	1.0
Sr	38	$[Kr]5s^2$	5.69, 11.02	1.0
Ba	56	$[Xe]6s^2$	5.21, 10.00	0.9
Ra	88	$[Rn]7s^2$	5.27, 10.14	0.9

The charge on the cations is +2 and the size of the ion is considerably smaller than the preceding alkali metals. Fajans' rules will predict that in the small sized beryllium and to some extent magnesium there will be a considerable degree of covalence and complexation. Be^{2+} ion neither occurs in solid state nor in solution. Beryllium chemistry is dominated by covalence and complexation. In the alkaline earths, however, the sizes of the cations have increased substantially to counter the effect of the charge. *The chemistry of the alkaline earths is, therefore, largely the chemistry of their ions.*

The electronegativities (Table 15.1) fall from beryllium to radium. For the alkaline earths the electronegativities are close to those for the alkalies but that of beryllium is comparatively high. In the formation of halides the electronegativity difference between the alkaline earths and the halogens is large enough to give ionic compounds. For beryllium substantial covalent character is predicted for the halides.

As expected the standard potentials of the elements become more negative down the group (Table 15.2). The increasing electropositive character with increasing atomic number is thus indicated.

Table 15.2. Some More Properties of Group IIA Elements

Element	Atomic Radius(A)	Ionic Radius (M^{2+}) (A)	M.P. (°C)	B.P. (°C)	Density (g/ml)	E°(volts) ($M^{2+}+2e \rightleftharpoons M$)
Be	1.11	0.31	1284	2507	1.84	−1.85
Mg	1.60	0.65	651	1103	1.74	−2.37
Ca	1.97	0.99	851	1440	1.54	−2.87
Sr	2.15	1.10	770	1320	2.60	−2.89
Ba	2.17	1.29	710	1500	3.50	−2.90
Ra	—	1.50	960	1140	~5	−2.92

The atomic and ionic radii (Table 15.2) are smaller than the preceding alkalies due to increase in nuclear charge. The metals have higher melting points than the alkalies. The two valence electrons of the group IIA make far stronger binding in the metallic state. Compared to the alkalies these elements have much higher densities since they have much smaller sized atoms.

15.1.2. Chemical Behaviour. In keeping with Fajans' rules the alkaline earth compounds are predominantly ionic. Beryllium compounds are covalent and magnesium assumes an intermediate role. The tendency towards complexation is highest in the smallest beryllium and gradually falls off in the series.

Hydrides: By virtue of their greater electropositive character the alkaline earths form ionic hydrides: CaH_2, SrH_2 and BaH_2. These are high melting, conducting in fused state and on electrolysis liberate hydrogen at the anode. These are obtained by the direct combination of hydrogen with the metals at ~200–400°C. Beryllium hydride is covalent and polymerised and magnesium hydride has properties intermediate between those of ionic and covalent hydrides.

Oxides: Beryllium oxide is polymeric and covalent. All the other oxides are ionic and have high melting points (Table 15.3). In general the tendency to form peroxides and superoxides increases along the group. Thus beryllium does not form any peroxide, magnesium only a peroxidated oxide $MgO_2.3MgO$ and the alkaline earths form monoxides, MO and peroxides MO_2. Calcium superoxide has been reported in about 8% yield as an admixture with calcium peroxide by reaction at 100°C between calcium peroxide and 30% H_2O_2.

Table 15.3. Melting Points of Some Compounds of Group IIA Elements

Compound	M. P. (°C)	Compound	M. P. (°C)
BeO	2570	$BeCl_2$	405
MgO	2800	$MgCl_2$	715
CaO	2572	$SrCl_2$	870
SrO	2430	$BaCl_2$	955

The oxides react in water to form hydroxides. The basic properties of the hydroxides increase, as expected, from beryllium to barium. Beryllium hydroxide is amphoteric and all the others are only basic. As expected from their high negative standard potentials calcium, strontium and barium readily react with cold water to form hydroxides with liberation of H_2. Magnesium reacts only on heating.

Halides: Beryllium halides are polymeric and covalent. These are non-conductors in fused state. The other halides are ionic in nature. In fused state they conduct electricity and they possess ionic crystal structure. Melting points of the chlorides appear in Table 15.3.

Nature of the aqueous solution: Since the complexing tendency decreases down the group from beryllium to radium it will only be logical to expect that the degree of hydration will fall in the same direction. Indeed the hydration energies fall from beryllium to barium and the ionic mobilities, for the same reason, increase from beryllium to barium. It is also interesting to observe that the hydration energies of group IIA metal ions, M^{2+}, are roughly five times larger than those of the preceding alkalies.

Table 15.4. Hydration Energies and Ionic Mobilities of Group IIA Elements

Property	Be	Mg	Ca	Sr	Ba	Ra
Ionic Radius (A)	0.31	0.65	0.99	1.10	1.29	1.50
Hydration Energy of M^{2+} (Kcal/mole)	570	460	395	355	305	—
Ionic mobility $\times 10^5$ (cm/sec/volt)	30	55.5	59.8	59.8	64.2	67

Nature of the solution in liquid ammonia: The alkaline earths dissolve in liquid ammonia to give ammoniated cations and ammoniated electrons. The molar extinction coefficient of the calcium solution is nearly double that of a sodium solution.

Complexes: We have already seen that beryllium is the most complexing in this group and that the complexing tendency decreases down the group. By virtue of a double charge on the cations the overall complexing ability of the alkaline earths is far greater than that of the monopositive alkalies. This is easily seen by these elements forming quite a number of complexes with strong polydenate ligands. For example, with 8-hydroxyquinoline (oxinH) magnesium readily forms an insoluble $[Mg(oxin)_2]$. This forms a basis for the gravimetric estimation of magnesium. Besides, both magnesium and calcium form soluble and stable complexes with EDTA (Chapter 10), which is the basis of the complexometric determination of water hardness. The alkaline earths form some poorly known acetylacetonate complexes. Their ammine complexes, such as $[Mg(NH_3)_6]Cl_2$, are weak and are easily dissociated into ammonia and the metal halide. The tendency of complexation dies down the group.

Recent studies with polycyclic ethers (called *crown ethers*) and poly macrocyclic ethers with nitrogen bridge heads (called *cryptands*) reveal that they are good complexing ligands for heavy alkaline earths like Sr^{2+} and Ba^{2+}. Such a cryptand is $N(CH_2\ CH_2O\ CH_2\ CH_2\ OCH_2\ CH_2)_3\ N(=L)$. Complexes of the type $[Sr/Ba\ (L)]\ SO_4$ have been characterised. (cf. page. 21). The metal ion is trapped inside the macrocyclic hole.

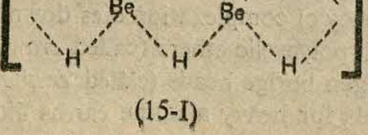
15.2. BERYLLIUM

15.2.1. General Considerations: Beryllium is the first member of group IIA. It has $[He]2s^2$ electronic configuration, has the highest ionisation potential in the group (9.32, 18.20 *e.v.*), has the highest electronegativity (1.5) in the group and has the smallest atomic (1.11A) and ionic radii (Be^{2+}, 0.31A). These properties of elementary beryllium make it a most suitable element for exhibiting covalent properties. Its complexing ability consequently is the highest in the group.

Beryllium chemistry is dominated by a tetrahedral geometry and to a lesser extent by a linear coordination. Beryllium is a member of the second period and hence can have no more than four orbitals (one *s* and three *p*'s) in the $n = 2$ quantum shell. This quantum shell does not have a *d*-orbital. Thus beryllium can have a maximum of four coordination and thus can attain the next noble gas configuration by complex formation. However four coordination can be attained either through a tetrahedral (sp^3 hybridisation) or a square planar (dsp^2) geometry. Since with beryllium the only *d*-orbital possible is the much higher energy 3*d*, square planar dsp^2 geometry is energetically unfavourable. For the linear coordination in beryllium we have to invoke an *sp* hybridisation giving two *sp* hybrid orbitals at 180° to each other (Chapter 5). Such a coordination does provide a valence shell of only $4 = (2 + 2)$ electrons around the metal. Hence beryllium tends to raise its coordination number to four allowing itself a noble gas configuration. Because of this tendency we find that the compounds with an apparent coordination number 2 (say $BeCl_2$) are really polymeric with a coordination number 4. The desire to attain noble gas configuration also makes beryllium a good acceptor. For example $BeCl_2$ readily forms addition compounds with neutral donors, giving compounds such as $BeCl_2.(OR_2)_2$.

It should be noted that the arguments advanced in favour of four-coordinate tetrahedral geometry in beryllium compounds are equally valid for other elements of the same period. Thus trivalent boron, quadrivalent carbon, trivalent nitrogen and bivalent oxygen also prefer a tetrahedral geometry to a square planar one.

15.2.2. Chemical Behaviour: *Hydrides:* The hydride of beryllium (BeH_2) and of magnesium (MgH_2) are intermediate between the ionic hydrides of lithium and sodium, and the covalent hydrides of the remaining elements in



(15-I)

these periods. These hydrides are solid polymerised molecules held together by hydrogen bridge bond comparable to that in diborane, B_2H_6. These hydrides are, therefore, not ionic and cannot conduct electric current. BeH_2 (15-I) appears to be more covalent than MgH_2 due to its smaller size and its electronegativity (1.5) being closer to that (2.1) of hydrogen. BeH_2 and MgH_2 are synthesised by the reaction of dimethyl beryllium/magnesium with lithium aluminium hydride in ether:

$$(CH_3)_2Be + LiAlH_4 \rightarrow BeH_2 + LiAlH_2(CH_3)_2$$
$$(CH_3)_2Mg + LiAlH_4 \rightarrow MgH_2 + LiAlH_2(CH_3)_2$$

Oxide and Hydroxide: Due to the small size and comparatively large charge of the beryllium ion BeO is covalent. Yet the compound has a high melting point (2570°C). This is due to the compound having a polymeric lattice rather than discrete covalent molecules. Each beryllium atom is tetrahedrally coordinated by oxygen. Beryllium does not form any peroxide or superoxide. Beryllium hydroxide is precipitated on the addition of OH^- ions to an aqueous solution of a beryllium compound. The hydroxide and the oxide are amphoteric. These dissolve in acids to give beryllium salts and in excess alkali to give beryllate ions:

$$Be(OH)_2 + 2OH^- \rightarrow BeO_2^{2-} + 2H_2O$$

Halides: Beryllium halides have rather low melting points (Table 15.3) and are non-conductors in fused state. The conductivity of fused beryllium chloride is about a thousandth of that of a fully ionised salt(say NaCl). These halides are polymeric and four covalent, polymerisation occurring through halogen bridging. Ordinary crystalline $BeCl_2$, which is polymeric, changes to a monomeric linear $BeCl_2$ form at ~750°C (Chapter 5). The anhydrous beryllium chloride dissolves very readily in water with large evolution of heat to form the tetrahydrate $BeCl_2.4H_2O$. This water is not lost over P_4O_{10} even over months, suggesting the tetraaquo structure $[Be(H_2O)_4]Cl_2$.

Beryllium fluoride cannot be obtained by neutralising beryllium hydroxide with HF since the fluoride hydrolyses on evaporation. It is obtained by igniting BeO in a stream of gaseous HF or better by heating fluoroberyllates. The chloride and the bromide are obtained by the action of halogens on a mixture of BeO and C or by the action of halogens on beryllium carbide. The iodide is best made by the action of HI on BeC_2.

Complexes: Complexing tendency of beryllium is reflected in the formation of polymeric species, in the strong hydration of its salts, in adduct formation of their halides and in the formation of a variety of neutral, cationic and anionic complexes. The class 'a' character of beryllium (Chapter 8) is exhibited by its readily forming complexes with nitrogen donors like ethylenediamine or with oxygen donors like water, acetylacetone etc. The coordination number in such complexes is always four and the stereochemistry of beryllium is tetrahedral.

A very interesting complex of beryllium is basic beryllium acetate $Be_4O(OOCCH_3)_6$. This is obtained by refluxing beryllium hydroxide with acetic acid. Other carboxylic acids also give similar complexes. The basic acetate is a crystalline but volatile substance, soluble in non-polar solvents. This is a non-electrolyte. The structure is now well established (Fig. 15.1). The four beryllium atoms complete a tetrahedron around the central and unique oxygen. The six carboxylate groups span the six edges of the tetrahedron. The compound has interlocking six-membered rings satisfying the tetrahedral bond angles of the four beryllium atoms. Note that each of the four beryllium atoms is also tetrahedrally coordinated to four oxygen. Three of these four oxygens come from the carboxylate groups and the fourth oxygen is the central, unique oxygen.

Another interesting manifestation of complexation is the increase in the solubility of insoluble BeO in water in the presence of $BeSO_4$. This is due to the replacement of the tetrahedrally disposed aqua molecules of $[Be(H_2O)_4]SO_4$ by four BeO units, the oxide oxygen forming a bond to the central beryllium (Fig. 15.2). The coordination around the BeO units is completed by three water molecules. The ultimate species in solution is $[Be(OBe(H_2O)_3)_4]^{2+}$.

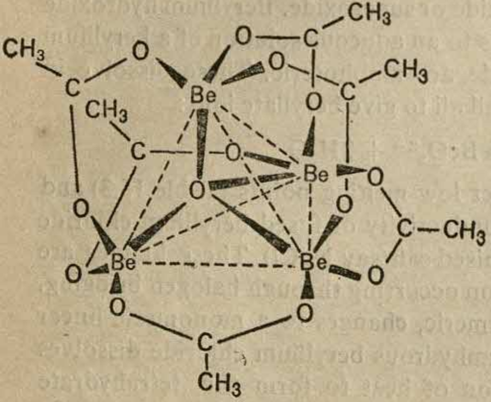


FIG. 15.1. Basic beryllium acetate

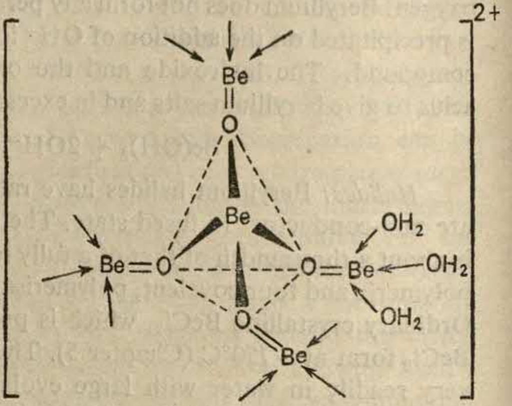
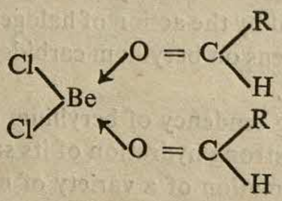


FIG. 15.2. The $[Be(OBe(H_2O)_3)_4]^{2+}$ ion

Beryllium halides act as Lewis acids giving adducts with aldehydes (15-II), ketones and ethers:



(15–II)

Complexes such as $[BeCl_2(dipy)]$, $[BeCl_2(o\text{-}phen)]$, $[Be(acac)_2]$ are also known.

Of the halocomplexes the fluoroberyllates, $[BeF_4]^{2-}$ are well-known. The complex $[BeCl_4]^{2-}$ is rather unstable. The fluoroberyllates can be made by dissolving BeO in concentrated solutions of ammonium bifluoride. The size of the $[BeF_4]^{2-}$ is comparable to that of $[SO_4]^{2-}$ and both the ions are tetrahedral. The two ions are, therefore, isomorphous. Just like the sulphate ion the fluoroberyllate ion also form Schönite type double fluoroberyllates: $M^I_2M^{II}(BeF_4)_2.6H_2O$.

15.3. COMPARISON OF BERYLLIUM AND ALUMINIUM: DIAGONAL RELATIONSHIP

Compared to beryllium, aluminium has a higher charge on its ion and also a higher size. The charge/radius ratio (Chapter 5) is almost the same for the two elements, and therefore they are of similar deforming power. Note that the charge/radius ratios of these two elements are far closer to each other than the lithium-magnesium pair. As a result the properties of beryllium/aluminium are much more similar than those of lithium/magnesium. Indeed beryllium/aluminium pair is hailed as the best diagonal pair in the Periodic Table.

	Be	Al
Charge on the ion	$+2$	$+3$
Ionic radius (A)	0.31	0.51
Charge/radius ratio	6.4	6.0

The points of similarities are:

1. Both the elements show strong tendency to covalence and complex formation. Aluminium halides are dimeric and covalent. Beryllium halides are polymeric and covalent. In aqueous solution the aquo ions are formed: $[Be(H_2O)_4]^{2+}$ and $[Al(H_2O)_6]^{3+}$.

2. Both beryllium hydroxide and aluminium hydroxide have amphoteric properties. Both betray basic properties in the presence of acids forming compounds like $BeSO_4$ or $Al_2(SO_4)_3$. Both the hydroxides dissolve in alkali to give beryllate and aluminate, although in aqueous solution these ions will have aqua molecules to complete their coordination zone.

$$Be(OH)_2 + 2OH^- \rightarrow BeO_2^{2-} + 2H_2O;\ Al(OH)_3 + OH^- \rightarrow AlO_2^- + 2H_2O$$

The beryllate and aluminate ions are also formed during dissolution of the metals in strong bases:

$$Be + 2OH^- \rightarrow BeO_2^{2-} + H_2\ ;\ Al + 2OH^- \rightarrow AlO_2^- + H_2$$

3. The standard potential of Be is -1.85 volts and that of Al is -1.66 volts, so that the metals should readily dissolve in acids to form metal salts. The dissolution proceeds best in HCl and H_2SO_4 and least in HNO_3.

4. Beryllium and aluminium occur together in nature in beryl $3BeO.Al_2O_3.6SiO_2$. Both Be and Al are isolated by electrolysis, the former from fused $BeCl_2$ and the latter from Al_2O_3. $BeCl_2$ is mixed with NaCl to bring it to the conducting (but unstable) form $[BeCl_4]^{2-}$.Al_2O_3 is dissolved in fused cryolite and then electrolysed.

15.4. RADIUM

In the early days of radioactivity Becquerel and the Curies noted that the uranium bearing mineral *pitchblende* was much too radioactive for its uranium content. They suspected that pitchblende contained elements which must be more radioactive than uranium. Painstaking extractions followed, and polonium and radium were discovered. Radium was found to be co-precipitated with barium sulphate showing that it belonged to group IIA alongwith the alkaline earths.

Pitchblende (mainly U_3O_8) is extracted with H_2SO_4. The extract is then treated with $BaCl_2$ when insoluble $BaSO_4$ carries alongwith it the small amount of radium as $RaSO_4$. The sulphate precipitate is fused with Na_2CO_3 and the mass extracted with HCl. Fractional crystallisation removes major amount of the more soluble $BaCl_2$ which is retained in solution. Repeated crystallisations give reasonably pure $RaCl_2$. Madame Curie electrolysed a solution of radium chloride with a mercury cathode. The resulting radium amalgam was then distilled to remove the mercury. Radium is a white metal which vigorously displaces hydrogen from water and rapidly tarnishes in air.

There are four natural isotopes of radium: radium-228, radium-226, radium-224 and radium-223. The half-lives are 6.7 years, 1590 years, 3.64 days and 162 days. Radium-228 is a beta-emitter and all others are alpha emitters. These radium isotopes are all members of the three radioactive disintegration series, the longest lived radium-226 being the decay product of the uranium-238 series.

Insofar as the chemistry of radium has been studied it resembles the alkaline earths in all respects. Radium chloride forms a dihydrate, isomorphous with barium chloride dihydrate. Radium sulphate is isomorphous with barium sulphate and is the least soluble sulphate in group IIA.

Principal use of radium salts is in radiotherapy. Radium salts are also used in luminous paints. For this purpose very minute quantities of radium salts are mixed with zinc sulphide, calcium sulphide or lithopone.

15.5. HARD WATER AND ITS SOFTENING

15.5.1. General Remarks: Water for common use often contains soluble salts of calcium and magnesium. These ions are capable of producing insoluble precipitates with soap material. Such water is termed hard water. Water, that has some soluble bicarbonates of calcium and magnesium, $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ that can be made to precipitate out by boiling as insoluble $CaCO_3$ and $MgCO_3$, is called *temporarily hard*. If the water contains soluble sulphates of calcium and magnesium, which are not precipitated on boiling, the water is said to be *permanently hard*.

Soap is a mixture of sodium salts of several fatty acids. These salts are soluble in water and are effective in bringing oils and greases from dirty linens into colloidal suspension in water. For simplicity, taking soap as sodium stearate, the following reaction occurs with calcium (or magnesium) ions:

$$2Na^+(C_{17}H_{35}COO)^- + Ca^{2+} \rightarrow \underset{\text{insoluble}}{Ca^{2+}(C_{17}H_{35}COO)_2^-} + 2Na^+$$

Unless all the calcium and magnesium ions are removed the soap fails to produce any lather with the water. On boiling only the temporary hardness can be removed but not the permanent hardness. Hard water can be made soft by passing it through beds of insoluble sodium aluminium silicate, technically called *zeolites* or synthetic cation exchange resins where these ions are retained and sodium ions are released from the zeolite or the resin bed (see also Chapter 17):

$$\text{Na}_2 \text{ zeolite} + \text{Ca}^{2+}(\text{or Mg}^{2+}) \rightarrow \text{Ca(or Mg) zeolite} + 2\text{Na}^+$$

The issuing water is free from Ca^{2+} or Mg^{2+} ions and is thus soft. However, the soft water now contains Na^+ ions. On prolonged use the zeolite has all its Na^+ ions replaced by Ca^+ or Mg^{2+} ions so that no more softening is possible. At this stage the calcium/magnesium zeolite is reactivated to sodium zeolite by running over it a concentrated solution of NaCl.

Water softening is also done by sodium hexametaphosphate $(NaPO_3)_6$ technically called *calgon*. Calgon is a highly soluble cyclic polyphosphate (Chapter 18). It binds calcium or magnesium in the form of a complex whose structure, however, is not very well established. A likely structure is shown in (18-XX). Some of the sodium ions of hexametaphosphate are replaced by calcium/magnesium ions:

$$\text{Na}_2[\text{Na}_4(\text{PO}_3)_6] + \text{CaSO}_4 \rightarrow \text{Na}_2[\text{Na}_2\text{Ca}(\text{PO}_3)_6] + \text{Na}_2\text{SO}_4$$

Another useful reagent in this respect is EDTA (Chapter 10), a celebrated sequestering agent. It is very effective in neutral or slightly acid solution. The hard deposits of insoluble salts in boilers and similar other equipments can be dissolved out by EDTA treatment.

It should be noted that while the zeolites and the ion-exchange resins give water free from calcium and magnesium ions by retaining them on the zeolite or the resin bed, EDTA and the hexametaphosphate sequester these ions as inactivated soluble EDTA or phosphato complexes. Regeneration of calgon or EDTA is not as simple as the regeneration of zeolites and the ion-exchange resins.

15.5.2. Ion Exchange Resins: As the very name suggests these constitute some resinous compounds which are capable of exchanging ions. Depending on the type of ions exchanged resins are termed cation exchange resins or anion exchange resins. A desirable property of the resins is their insolubility in common solvents. Thus a cation exchanger has to be a substance with polymeric anion but with small exchangeable cations while an anion exchanger has to have a polymeric cation with small exchangeable anions:

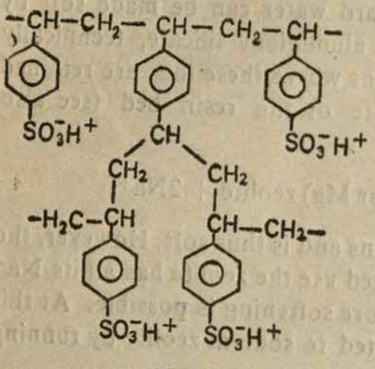
Cation Exchanger = (Resin anion$^-$) B^+

(Resin anion$^-$) B^+ + C^+ (solution) $\rightleftharpoons$ (Resin anion$^-$) C^+ + B^+ (solution)

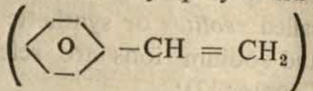
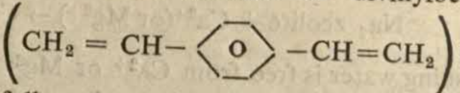
Anion Exchanger = (Resin cation$^+$) A^-

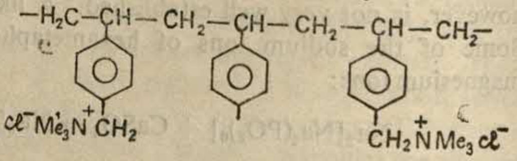
(Resin cation$^+$) A^- + C^- (solution) $\rightleftharpoons$ (Resin cation$^+$) C^- + A^- (solution)

The above equilibria may be shifted this way or that way by using suitable concentration of ions in solution. It follows that the original resins can be regenerated by treating with a solution containing appropriate ions.



(15-IV)

A common synthetic cation exchange resin (15-IV) is obtained by polymerisation of styrene  and a small amount of divinylbenzene  being followed by sulphonation. Note that in the resin (15-IV) H^+ is the exchangeable cation, the rest is the enormously bulky, insoluble, polymeric resin anion backbone. If we treat this resin with Na^+ ions its H^+ will be replaced by Na^+ and we will have a sodium form cation exchanger. An anion exchange resin is a polymer having amine or quaternary ammonium groups contained in a polymeric network (15-V). The resin is made by polymerisation of styrene and divinylbenzene and the product is then chloromethylated. The product is next treated with trimethylamine. In this resin chloride ion is the exchangeable ion, the rest being a non-exchangeable, bulky, polymeric cation. By treatment with proper anions we can convert this resin to the hydroxide form, sulphate form, nitrate form, etc.



(15-V)

When hard water is allowed to pass through a bed of a cation exchanger the Ca^{2+}/Mg^{2+} ions of hard water are exchanged. The solution now contains the cations present originally in the resin. Synthetic cation exchange resins are superior to the natural or artificial zeolites for water softening because the synthetic resins can be regenerated many more times than it is possible with the zeolites.

If we have two columns of ion exchange resins—one containing a H^+ form cation exchanger and the other containing an OH^- form anion exchanger—and if we let ordinary water pass through the columns in succession we will finally get *deionised water.*

$$MgSO_4 + 2H^+ (resin)^- \rightarrow H_2SO_4 + (Mg\ resin)$$
$$H_2SO_4 + 2OH^- (resin)^+ \rightarrow 2H_2O + (resin\ SO_4)$$

15.6. COMPOUNDS OF MAGNESIUM AND THE ALKALINE EARTHS

15.6.1. Magnesium Sulphate: This occurs in nature as the heptahydrate called *Epsom salt* or *episomite* and as the monohydrate *kieserite*, $MgSO_4.H_2O$.

Most of the commercial heptahydrate salt is obtained from magnesite, $MgCO_3$ by treating with dilute sulphuric acid and crystallising. The heptahydrate has its six water molecules coordinated to Mg^{2+} and the seventh water molecule being hydrogen bonded to the sulphate radical.

When a solution of magnesium sulphate (or any other soluble magnesium salt) is treated with alkali carbonate solution, a precipitate of magnesium carbonate and hydroxide is obtained. This light but voluminous precipitate is mixed with ~ 15% asbestos fibre and the mixture is widely used as an insulating material for boilers and steam pipes. Magnesium sulphate is also used as a mild purgative.

15.6.2. Magnesium Chloride: This is extracted from carnallite $KCl.MgCl_2.6H_2O$ with a hot 20% solution of $MgCl_2$. On concentrating and cooling KCl first crystallises. The mother liquor on further concentration gives crystals of $MgCl_2.6H_2O$. The chloride may also be obtained from the carbonate by HCl treatment. Anhydrous magnesium chloride cannot be obtained by simply heating the hexahydrate since hydrolysis occurs:

$$MgCl_2 + H_2O \rightleftharpoons Mg(OH)Cl + HCl$$

Heating in an atmosphere of HCl gas provides the anhydrous salt. Presence of HCl gas suppresses the above possible hydrolysis.

15.6.3. Sorel's Cement or **Zyolith:** Magnesium carbonate decomposes at ~700°C to MgO and CO_2. The resulting fluffy powder consisting of MgO and little $MgCO_3$ is known as 'light-burnt magnesia'. When a concentrated solution of magnesium chloride is mixed with light-burnt magnesia the paste sets to a hard marble-like mass called *Sorel's cement* or *Zyolith*. This is used as a substitute for tile.

15.6.4. Magnesium Perchlorate: This is obtained by the action of $HClO_4$ on magnesium carbonate. The anhydrous perchlorate is a very efficient drying agent, and is known as *anhydrone*.

15.6.5. Plaster of Paris: This is calcium sulphate hemihydrate, $CaSO_4.\frac{1}{2}H_2O$ or $(CaSO_4)_2.H_2O$. This is obtained commercially by careful heating of gypsum $CaSO_4.2H_2O$ to 120-130°C. The heating is generally done in large steel pots provided with mechanical stirrers or in rotary kilns. When plaster of Paris is mixed with water to a paste it sets in a few minutes to a solid mass owing to rehydration. It is used in the preparation of moulds for casting metals and for making casts for statues and also in surgical settings.

15.6.6. Calcium Carbide: This is an ionic carbide. This is manufactured by heating a mixture of quicklime (CaO) and coke to a high temperature (~3000°C) in an electric furnace:,

$$CaO + 3C \rightarrow CaC_2 + CO$$

From time to time fresh mixture of quicklime and coke is introduced into the furnace from the top. Electric arc is set in the lower part of the furnace and above the arc region there are air inlets to burn the CO. The heat produced during the burning of CO in air helps in preheating the incoming charge of CaO and C. The calcium carbide collects at the bottom of the furnace and is tapped off from time to time. Calcium carbide is used in the preparation of acetylene ($CaC_2 + 2HCl \rightarrow CaCl_2 + C_2H_2$), in oxy-acetylene flame, as an illuminant and in the manufacture of calcium cyanamide—a nitrogenous fertiliser:

$$CaC_2 + N_2 \rightarrow CaN.CN + C$$

15.6.7. Calcium Cyanamide: This is manufactured by heating finely divided calcium carbide at ~1000°C in an atmosphere of nitrogen:.

$$CaC_2 + N_2 \rightarrow CaN.CN + C$$

The resulting black mixture of calcium cyanamide and carbon is known as *nitrolim*. This is used in the synthesis of ammonia. On treating nitrolim with steam under pressure, calcium carbonate and ammonia are produced:

$$CaNCN(+C) + 3H_2O \rightarrow CaCO_3 + 2NH_3(+C)$$

Calcium cyanamide is used as a fertiliser. In the soil it is converted by a series of reactions to nitrate—a form assimilable to plants.

15.6.8. Bleaching Powder: A detailed discussion on the synthesis, properties and uses of this important commercial product appears in 20.7.2.

15.6.9. Barium Chloride: It is manufactured by strongly heating a mixture of *heavy spar* ($BaSO_4$), coke and calcium chloride:

$$BaSO_4 + 4C + CaCl_2 \rightarrow BaCl_2 + CaS + 4CO$$

The mass is extracted with water, concentrated and the barium chloride crystallised. Some calcium sulphide that might be retained in solution is precipitated as CaS.CaO by the addition of little lime.

15.6.10. Lithopone: A mixture of $BaSO_4$ and ZnS obtained by mixing barium sulphide with zinc sulphate

$$BaS + ZnSO_4 \rightarrow BaSO_4 + ZnS$$

is known as lithopone. This is a valuable white pigment. It does not blacken in H_2S atmosphere. But it slightly darkens in light due to liberation of metallic zinc. However while in the dark it is converted to the oxide, thus recovering its whiteness.

15.7. ISOLATION OF THE GROUP IIA ELEMENTS

15.7.1. Beryllium: Beryllium occurs in nature mostly as *beryl*, $Be_3Al_2(SiO_3)_6$ (= $3BeO.Al_2O_3.6SiO_2$) and also as crysoberyl, BeO, Al_2O_3. Beryl is usually fused with K_2CO_3, the melt digested with H_2SO_4 and water. Silica is removed by filtration, the filtrate concentrated and cooled when potassium aluminium alum crystallises. The remaining liquor is then treated with ammonium carbonate to remove any aluminium or trace of iron. The filtrate then deposits on boiling basic beryllium carbonate, which on ignition gives BeO. This oxide dissolves in sulphuric acid from which $BeSO_4.4H_2O$ can be crystallised. Passage of chlorine over a heated mixture of BeO and carbon gives $BeCl_2$ which sublimes. For extraction of the metal $BeCl_2$ is fused with sodium chloride (or BeF_2 fused with NaF) and the melt is electrolysed in a watercooled nickel or iron crucible (cathode) with a carbon anode. Beryllium is deposited on the cathode A typical charge is 25 Kg. NaCl to 5 Kg. $BeCl_2$. The NaCl is first fused and then hydrogen is introduced as a protective measure against any oxidation. $BeCl_2$ is then introduced in small amounts. Temperature is around 725-800°C. The beryllium metal deposited on the cathode as flakes is protected by the fused electrolyte. After electrolysis the mass is leached with water, the metal washed with alcohol and dried:

$$BeCl_4^{2-} \rightarrow Be^{2+} + 4Cl^-$$

$$Be^{2+} + 2e \rightarrow Be; 2Cl^- \rightarrow Cl_2 + 2e$$

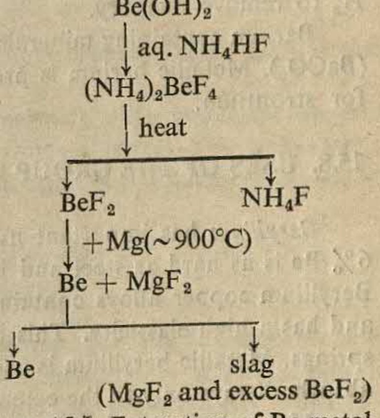


Chart 15-I. Extraction of Be metal from $Be(OH)_2$

Metallic beryllium has also been obtained by magnesium reduction of BeF_2 (Chart 15-I)in a furnace $\sim$900°C. The metal is finely dispersed in a slag consisting of MgF_2 and excess BeF_2. Leaching with water provides the metal.

15.7.2. Magnesium: The best source of magnesium is carnallite, $KCl.MgCl_2.6H_2O$. This is fused and electrolysed in an iron crucible serving as the cathode and a hanging carbon rod as the anode. The carbon rod is enclosed in a porcelain jacket. Magnesium liberated at the cathode floats at the surface of the melt and is protected from atmospheric oxygen by a current of hydrogen or coal gas. The chlorine liberated at the anode escapes through a side tube in the porcelain jacket.

Sea water is also a good source of magnesium ($\sim$0.13%). Sea water is treated with $Ca(OH)_2$ when less soluble $Mg(OH)_2$ is precipitated. $Mg(OH)_2$ is filtered and dissolved in HCl. The resulting solution is concentrated when $MgCl_2.6H_2O$ crystallises. This is fused and electrolysed as described above. The chlorine gas is converted to HCl which is then returned to the process.

15.7.3. Calcium, Strontium and Barium: Calcium is found in nature in several forms: *limestone*, *chalk*, *marble* ($CaCO_3$); *dolomite* ($CaCO_3.MgCO_3$); *anhydrite* ($CaSO_4$); *gypsum* ($CaSO_4.2H_2O$); *phosphorite* ($Ca_3(PO_4)_2$); *fluorspar*

(CaF_2). It is obtained on a commercial scale by electrolysis of fused $CaCl_2$. Some CaF_2 is added to lower the temperature of fusion (780°C). The elctrolysis is carried out in a graphite pot serving as the anode. A water cooled iron cathode hangs into the fused electrolyte. As electrolysis proceeds metallic calcium is deposited on the cathode in the form of a rod, and the cathode is slowly screwed up. A layer of fused electrolyte protects the metal from oxidation.

Important strontium bearing minerals are *celestine* ($SrSO_4$) and *strontianite* ($SrCO_3$). Strontium is not made on a commercial scale but may be obtained by following a procedure parallel to that of calcium extraction. Alternatively electrolysis with a mercury cathode gives strontium amalgam, which can be heated in H_2 to remove mercury.

Barium containing minerals are *barytes* or *heavy spar* ($BaSO_4$) and *witherite* ($BaCO_3$). Metallic barium is produced by procedures analogous to those used for strontium.

15.8. USES OF THE GROUP IIA ELEMENTS

Beryllium has important uses in alloys. A copper-beryllium alloy with ~ 6% Be is as hard as steel and has a high chemical and mechanical resistivity. Beryllium-copper alloys containing ~ 2% Be and ~ 0.5% Ni is also very hard and has a high elasticity. This alloy is used in the manufacture of high grade springs. Metallic beryllium is used in making windows for X-ray tubes since it absorbs X-rays only to the extent of one-seventeenth of that by aluminium.

Magnesium alloys are light and are used in aircraft and automobile parts *Magnalium* is a magnesium aluminium alloy with 10-30% Mg. Other elements with which alloys have been made are Zn, Mn, Sn, Zr. Magnesium is a good and useful reducing agent. Magnesium turnings are used to reduce UF_4 in graphite-lined steel reactors to produce uranium metal.

Calcium is a powerful reducing agent. It is often used in the preparation of metals whose oxides are resistant to reduction. Metallic calcium is used in the production of certain lead alloys. A lead alloy containing 0.7% Ca, 0.6% Na and 0.04% Li is used as a bearing metal.

15.9. ANALYTICAL REACTIONS OF THE GROUP IIA ELEMENTS

Beryllium accompanies aluminium in group IIIA of the qualitative scheme of analysis. Be and Al form soluble beryllate and aluminate respectively. But the beryllium solution alone on dilution and on boiling precipitates $Be(OH)_2$. Beryllium can be distinguished from aluminium by its reaction towards 8-hydroxyquinoline. The aluminium compound $[Al(oxin)_3]$ is insoluble in dilute acid while the beryllium oxinate is soluble. Beryllium is usually estimated quantitatively by igniting the hydroxide to BeO and weighing.

Magnesium appears in group V of the qualitative scheme. After the separation of the alkaline earths as carbonates magnesium is usually precipitated as magnesium ammonium phosphates (from a slightly ammoniacal solution) which can be ignited to $Mg_2P_2O_7$ and then weighed. Magnesium can also be precipitated as $[Mg(oxin)_2]$ with 8-hydroxyquinoline. It can be weighed directly. Alternatively it can be dissolved in dilute HCl and treated with an excess of KBr. The solution is then titrated with a standard potassium bromate solution in the presence of methyl orange serving as indicator. Each oxine group reacts with four equivalents of bromine to give 5, 7-dibromoxine:

$$C_9H_7ON + 2Br_2 \rightarrow C_9H_5ONBr_2 + 2H^+ + 2Br^-$$

So $[Mg(oxin)_2]$ reacts with 8 equivalents of bromine which comes from the reaction of potassium bromate and bromide:

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

The end point is marked by the discharge of methyl orange colour due to oxidation by bromine.

One mole $KBrO_3$ gives six bromine atoms so that its equivalent weight is one-sixth of its molecular weight. Further since one $[Mg(oxin)_2]$ is equivalent to eight bromine atoms we have 1 Mg ≡ 8 Br so that one equivalent of $KBrO_3$ corresponds to one-eighth of magnesium:

$$1000 \text{ ml. N } KBrO_3 \equiv 1/8 \times 24.32 \text{ gm Mg}$$

$$1 \text{ ml. N } KBrO_3 \equiv 0.003040 \text{ gm Mg}$$

Calcium, strontium and *barium* appear in group IV of the qualitative scheme and are precipitated as carbonates. Sr/Ba are converted to sulphates and are identified by flame colouration (Ca, brick red and Ba, apple green). Calcium is determined quantitatively by first precipitating as oxalate and titrating the oxalate against $KMnO_4$. Sr and Ba are determined gravimetrically as sulphate.

Calcium and magnesium estimation in hard water is nowadays rapidly done by titrating the water complexometrically with disodium salt of EDTA in the presence of a suitable metal indicator (Chapter 10).

STUDY QUESTIONS

1. Compare and contrast the alkalies and the alkaline earths under the heads: (*a*) electronic configuration (*b*) ionisation potential (*c*) valence (*d*) standard electrode potential and (*e*) chemical behaviour.

2. Beryllium chemistry is much different from that of the alkaline earths. This is due to the small size of beryllium. Comment.

3. Beryllium is four-coordinated and tetrahedral. Comment. Do you consider that this will be valid for B, C and N also ?

4. The elements of group IA and IIA do not give variable valences. Discuss.

5. Discuss the diagonal relationship between Be and Al.

6. Comment on the trend of the hydration energies and ionic mobilities of Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}. Also comment on the hydration energies (Kcals/mole) of the following pairs of ions of similar size:

$Li^+(121)$, $Mg^{2+}(460)$; $Na^+(95)$, $Ca^{2+}(395)$; $K^+(76)$, $Ba^{2+}(305)$

7. Explain what is meant by 'hard water'. Outline a modern technique of determining hardness of water. How can we remove the hardness ?

8. Indicate in which direction the following changes occur in group IIA:
   (*a*) The cations become more strongly hydrated
   (*b*) The size of the M^{2+} ions decreases
   (*c*) The hydroxides become less soluble in water
   (*d*) The salts become more soluble in organic solvents
   (*e*) Complexation increases
   (*f*) The standard potentials become more negative

9. Give a concise account of the cation and anion exchange resins. How would you proceed to obtain a sample of de-ionised water using these resins ?

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16

Group IIIB. Boron, Aluminium, Gallium, Indium and Thallium

The five elements boron, aluminium, gallium, indium and thallium comprise group IIIB of the Periodic Table. The percent abundances of the elements in the earth's crust are: B(0.003%); Al(8.0%); Ga(0.0004%); In (0.00001%); Tl (0.00001%).

Boron occurs in small amount due to its nucleus being disintegrated by natural bombardment reactions. Aluminium is very abundant and occupies the third position after oxygen (46.6%) and silicon (27.7%). The abundance of the other three elements is poor and falls from gallium to the other two.

16.1. COMPARATIVE STUDY OF THE GROUP IIIB ELEMENTS

16.1.1. General Considerations: Considerable changes occur on moving from group IIA to group IIIB. All the elements have an outer quantum shell arrangement of s^2p (Table 16.1). Underneath this s^2p subshells boron and aluminium alone have noble gas electronic configurations but gallium, indium and thallium have filled *d*-shells. This seems to influence the properties of the elements.

Table 16.1. Electronic Configurations and some Properties of Group IIIB Elements

Element	Atomic Number	Electronic Configuration	Ionisation Potential (*e.v.*)	Electro-negativity
B	5	$[He]2s^22p^1$	8.29, 25.15, 37.92	2.0
Al	13	$[Ne]3s^23p^1$	5.98, 18.82, 28.44	1.5
Ga	31	$[Ar]3d^{10}4s^24p^1$	6.00, 20.51, 30.70	1.6
In	49	$[Kr]4d^{10}5s^25p^1$	5.78, 18.86, 28.03	1.7
Tl	81	$[Xe]4f^{14}5d^{10}6s^26p^1$	6.10, 20.42, 29.8	1.8

The first ionisation potentials are slightly lower than those of group IIA, possibly because the electron is lost from a 2*p* orbital in group IIIB compared to the filled 2*s* orbital in group IIA. However the three successive ionisation potentials taken together make the energy too large to be compensated by lattice energy released in the formation of ionic crystals. Taking the case of boron, the charge/radius ratio is 15 whereas that for the preceding beryllium is only 6.4. Thus it is no wonder that boron chemistry is dominated by covalence. As we descend the group the ionisation potentials decrease in aluminium but the charge/radius ratio is still high (6.0). Aluminium has also a dominant covalent chemistry. The decrease in ionisation potentials from boron to aluminium may also be interpreted to mean that under favourable circumstances aluminium can form some ionic compounds as well. Unlike groups IA and IIA, the ionisation potentials do not show a regular decrease from boron to thallium; instead gallium, indium and thallium have very close potentials. The sizes of these three elements do not vary significantly. An explanation must be sought in the pseudo noble gas configurations underneath the outer valence shell. Fajans' rules say that such elements are more liable to deformation than those with noble gas configurations.

In a group of regular elements the standard electrode potentials normally become more negative with increasing atomic number. But that does not seem to hold in the series aluminium to thallium (Table 16.2), once again suggesting that pseudo noble gas core is more deformable than a noble gas core.

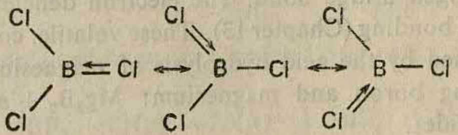
Table 16.2. Some More Properties of Group IIIB Elements

Element	Atomic Radius(A)	Ionic (M^{3+}) Radius(A)	M.P. (°C)	B.P. (°C)	Density (g/ml)	$M^{3+} + 3e \rightleftharpoons M$; $E°$(volts)
B	0.88	0.20	~2200	2550	2.31	—
Al	1.26	0.52	660	2270	2.7	−1.66
Ga	1.26	0.60	29.8	2030	5.93	−0.53
In	1.44	0.81	157	2100	7.29	−0.34
Tl	1.48	0.95	304	1460	11.85	+0.72

With two electrons in an *s* orbital and one in a *p* orbital, there is a case for showing monovalence in addition to the group valence. But boron never exhibits +1 oxidation state but only a consistent +3 state. This trivalent state in boron is exemplified in non-electrolytic compounds of the form BX_3, the three covalent bonds involving the three equivalent sp^2 hybrid orbitals at 120° to each other in the same plane. Three covalent bonds offer to boron a mere sextet, two electrons short of an octet. This makes boron an electron deficient element. The story of boron is, thus, the story of an electron deficient element. This character makes boron compounds very efficient Lewis acids, that is, electron acceptors (Chapter 8). A large number of stable adducts of boron halides with amines, ethers, sulphides, etc. are formed with evolution of large amount of heat. In these adducts boron attains a four covalent tetrahedral (sp^3) structure. The triangular planar (sp^2) BX_3 molecule gets distorted to a pyramid so that the empty *p* orbital of boron now becomes an sp^3 orbital. This orbital then forms a bond with the lone pair from the donor amines, ethers etc. Electron deficiency makes boron form unique *hydrogen bridge bond with three centres but with two electrons* (Chapter 13). This unique character also explains its tendency to receive back coordinated electron, to form π-bonds with elements like Cl, F etc. Boron in BCl_3, BF_3 etc could have attained noble gas configuration through dimerisation (compare Al_2Cl_6) (16-II) but it does not. The boron-halogen bonds are shorter than single bonds. The three sp^2 hybrid orbitals form three electron-pair bonds with three halogens and the third *p* orbital receives a back donated pair of electrons from a filled *p* orbital of a halogen. Since all the three boron-halogen distances are

$$\mathrm{B}\ \underset{2s}{\underline{\uparrow\downarrow}}\ \ \underset{2p}{\underline{\uparrow}}\ \ \underset{2p}{\underline{\quad}}\ \ \underset{2p}{\underline{\quad}}\ \ \text{hybridises to}\ \ \underset{2(sp^2)}{\underline{\quad\uparrow\quad}}\ \ \underset{(2(sp^2)}{\underline{\quad\uparrow\quad}}\ \ \underset{2(sp^2)}{\underline{\quad\uparrow\quad}}\ \ \underset{2p}{\underline{\quad}}$$

short and equivalent it can only mean that the real structure is a resonance hybrid of the following structures (16-I):



(16-I)

The trend of multiple bond formation falls sharply in aluminium and other members. This is due to an increase in the size of the central element. Overlap of a larger aluminium orbital with a chlorine orbital over a longer internuclear distance gives a weaker bond. Also both aluminium and chlorine have more filled inner orbitals, which tend to repel. This fall in multiple bond formation with increasing atomic number in a group is a general feature of the Periodic Table. As we move to aluminium there is still enough covalent trend which is reflected in dimeric covalent structures of the aluminium halides, Al_2X_6. Only in the fluoride sufficient ionic character appears. The ability to behave as Lewis acid falls off in the order B>Al>Ga>In~Tl. Halides of gallium, indium and thallium also show dimerisation. In contrast to boron there is a well defined aqueous cationic chemistry of Al, Ga and In being exemplified by $[Al(H_2O)_6]^{3+}$ and $[In(H_2O)_6]^{3+}$.

Although monovalence is not of importance in boron or aluminium it gains in importance down the group. With thallium +1 oxidation state becomes the dominating feature of its chemistry. The lower valence becomes increasingly important due to the so-called *inert pair effect*. The two *s* electrons of the s^2p outer shell become resistant to some chemical reagents, and are neither easily lost nor do they easily participate in covalent bond formation. In this +1 oxidation state, too, gallium, indium and thallium do not show any gradation in properties. Their first ionisation potentials are nearly the same (5.79—6.11 *e.v.*) so that there is no spectacular enhancement in basic properties down the group. Thallium

(III) solutions are not stable in the presence of metallic thallium. The equilibrium $Tl^{3+} + 2Tl \rightleftharpoons 3Tl^{+}$ proceeds almost to completion.

The extremely high melting point of boron indicates very strong binding forces. Aluminium is comparatively soft. It has a true metallic lattice and has a high conductivity. Gallium is a liquid over a wide range ~2000°C, which has made possible its use in high temperature thermometry.

16.1.2. Chemical Behaviour: The chemical behaviour will be discussed under two heads: trivalent state and the monovalent state.

A. Trivalent State: This is the group valence and all the three electrons in the s^2p outer shell are utilised. In boron the covalent state is important. The tendency to complexation is decidedly the highest in boron. This trend decreases in aluminium and the later members but not in a graded manner.

Hydrides: The boron hydrides are also called *boranes* and are designated usually by the number of boron atoms: B_2H_6 (diborane), B_4H_{10} (tetraborane), B_5H_9 (pentaborane (9)), B_5H_{11} (pentaborane (11)) etc. These are remarkable in their forming hydrogen bridge bond. The electron deficient character of boron leads to such special bonding (Chapter 13). These volatile, covalent hydrides were originally synthesised by the acid hydrolysis of magnesium boride which was obtained by heating boron and magnesium: $Mg_3B_2 + \text{acid} \rightarrow$ a mixture of several boron hydrides.

The volatile hydrides were collected in liquid-air traps and then purified by fractional distillation. Thus the boron hydrides B_4H_{10}, B_5H_9, B_6H_{10} and $B_{10}H_{14}$ were isolated. In these compounds there are *three centred two electron bonds* alongwith usual two electron two centred covalent bonds. For structure of diborane, B_2H_6, see Chapter 13.

The aluminium hydride *alane* is a polymeric species $(AlH_3)n$. This also has hydrogen bridging. Evidences for *gallane* are not convincing. Great chemical reactivity of alane and gallane make their syntheses by hydrolysis reactions difficult. They are made by subjecting a mixture of trialkyls $Al(CH_3)_3$ and hydrogen to high voltage electric glow discharge. The group IIIB hydrides form many complex compounds with donor groups such as ammonia, amines, ethers as also hydride ions. Complex anionic hydrides like lithium borohydrides ($LiBH_4$), lithium aluminium hydride ($LiAlH_4$) and lithium gallium hydride ($LiGaH_4$) are well-known.

Oxides and Hydroxides: The hydroxide of boron, $B(OH)_3$, is a definite weak acid (H_3BO_3) with no basic properties. Orthoboric acid, H_3BO_3, is a tribasic acid with $K_A^I \sim 6 \times 10^{-10}$, $K_A^{II} \sim 1.8 \times 10^{-13}$ and $K_A^{III} \sim 3 \times 10^{-14}$. Its acidity is greatly raised by the addition of certain polyhydroxy compounds like glycerol due to the formation of complex acids. On passing from boron to aluminium we find the hydroxide to be amphoteric and reacting in several ways: (1) as an acid ($H[AlO_2]$ or $H_3[Al(OH)_6]$) forming metallic aluminates; (2) as a base $Al(OH)_3$ giving ionised salts with aluminium as a hydrated cation; (3) forming neutral, covalent derivatives $AlBr_3$, $Al(C_2H_5)_3$ etc. Gallic hydroxide is amphoteric but on the whole it is a weaker base but stronger acid than aluminium hydroxide, forming neutral gallates M^IGaO_2. Indium behaves in the same way giving indates M^IInO_2. But thallic hydroxide is not amphoteric but only basic, although only a weak one. The addition of alkali to solutions of gallic and indic salts first precipitate their hydroxides which dissolve on addition of more alkali but with thallic salt the hydroxide does not dissolve on addition of excess alkali.

The boric oxide B_2O_3 is obtained by fusing boric acid. With water it forms boric acid and it readily reacts with other metal oxide to give metal borates. The formation of some coloured metal borates is a common reaction employed in detection of metal ion. Aluminium oxide, Al_2O_3, can assume different crystal structures depending on the mode of preparation. Gallium oxide also exists in more than one form and so also Tl_2O_3. Like boron, aluminium, gallium and thallium form mixed oxides, with other metal oxides.

Halides: Boron halides are known for all the halogens. These are all covalent and monomeric. In keeping with the normal behaviour the boiling points increase with increasing molecular weights of the halides:

Halide	BF_3	BCl_3	BBr_3
B. P. (°C)	−101	12.5	90

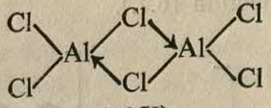
These are readily hydrolysed by water forming boric acids, and for the fluoride also fluoroboric acid:

$$4BF_3 + 6H_2O \rightarrow 3H_3O^+ + 3BF_4^- + H_3BO_3$$
$$BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl$$

These are all strong Lewis acids, and form numerous addition compounds:

$$BF_3 + N(CH_3)_3 \rightarrow F_3B \leftarrow N(CH_3)_3$$
$$BF_3 + OR_2 \rightarrow F_3B \leftarrow OR_2$$

Among the halides of Al, Ga, In and Tl, the fluorides are all expected to be ionic with high melting points. However it has recently been shown that these have polymeric covalent six coordinated structures with all the fluorine atoms being bridging in nature (cf: Part I, p. 342). The other halides are largely covalent, and attain octet through dimerisation (16-II). The dimeric structures are retained in non-polar solvents such as benzene but in water they break down,

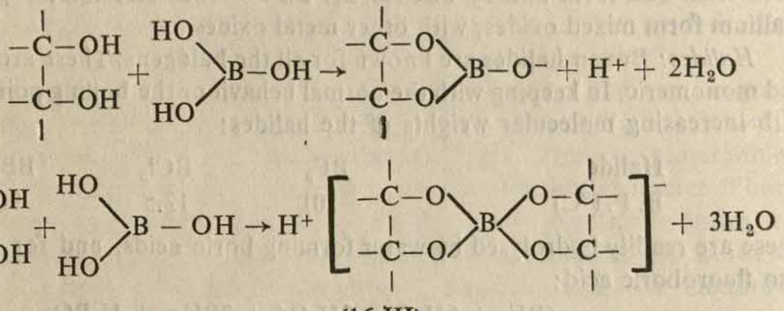


(16-II)

being assited by a large solvation energy, into the hexaaquo ions ($[M(H_2O)_6]^{3+}$). The dimers also break down while reacting with other donor centres (Lewis bases) forming adducts of the type $(CH_3)_3N \rightarrow AlCl_3$. The stability of such adducts falls off from boron to gallium.

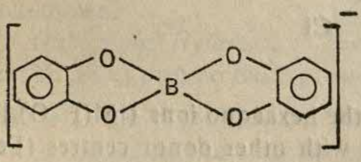
Alums: Aluminium, gallium, indium and thallium form double sulphates $M^I M^{III} (SO_4)_2.12H_2O$ where M^I is a univalent cation NH_4^+, Cs^+ etc. (page 62).

Complexes: In addition to the tetrahedral hydride and halide complexes $Li[AlH_4]$ and $H[BF_4]$ already mentioned, many octahedral halocomplexes are known such as $[GaCl_6]^{3-}$, $[InCl_6]^{3-}$ and $[TiCl_6]^{3-}$. The increase in coordination number from four in boron to six in the later elements is due to increased size whereby more groups can be packed around the metal. The acceptor property of boron is noted in adduct formation of boron halides with Lewis bases. An interesting case of complexation tendency of boron is shown in the enhanced acid character of boric acid in the presence of polyhydroxy compounds. Addition of mannitol, glycerol, etc. makes it a far stronger acid. Mannitol group coordinates to boron (16-III), makes its weakly acidic H^+ a strong acid and makes titration with sodium hydroxide possible to a phenolphthalein end point. A mono-chelate or a dichelate may be formed; in both cases one H^+ is liberated.

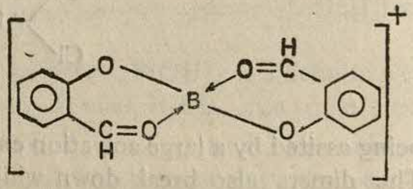


(16-III)

The tendency to chelation by boron is also revealed in the formation of complexes with catechol (16-IV), salicylaldehyde (16-V) etc. The former is an example of an anionic boron complex and the latter a cationic boron complex. The boron salicylaldehyde complex has been resolved into optical isomers thus indicating a tetrahedral stereochemistry. Acetylacetone (acacH) reacts with boron halides to give cationic bis (acetylacetonato) complex $[B(cacac)_2]X$. Non-electrolytic complexes like $[BF_2(acac)]$ are also known. Note that in all its complexes boron is consistently four-coordinate tetrahedral. The other elements also form tris (chelate) complexes, for example with acetylacetone, oxalate or with 8-hydroxyquinoline. The last named ligand is commonly utilised for gravimetric estimation of aluminium (Chapter 10; Section 16.7.).



(16-IV)



(16-V)

B. Monovalent State: This oxidation state gains importance only with the heavier elements of the group. The monovalent state of aluminium is suspected from the studies of anodic oxidation of aluminium. Hydrogen evolution at the cathode and the dissolution of aluminium at the anode are not in conformity with Faraday's law. Monovalent gallium compounds have been claimed to be formed by thermal dissociation of trivalent compounds:

$$GaCl_3 \overset{1100°C}{\rightleftharpoons} GaCl + Cl_2$$

Compounds of the empirical formula GaX_2(X = halogen) indicating apparently an oxidation number of +2 for gallium are really $\overset{I}{Ga}[\overset{III}{Ga}X_4]$. These are obtained by the general reaction:

$$2Ga + 4GaX_3 \rightarrow 3\overset{I}{Ga}[\overset{III}{Ga}X_4]$$

With thallium the +1 oxidation state is well characterised. The element is commercially available in thallous state. The low charge on the cation and comparatively large size confers on the ion enough properties to make its chemistry resemble those of the alkalies and silver. The thallous compounds are nearly all salts. Interestingly the ionic mobility is comparable to those of the alkalies and silver:

Ion	Tl^+	K^+	Rb^+	Cs^+	Ag^+
Ionic Radius (A)	1.44	1.33	1.48	1.69	1.26
Ionic mobility × 10^5 (cm/sec/volt)	65.6	64.2	67.2	68.0	54.3

The other similarities are: the ion is colourless, the hydroxide TlOH is very soluble in water and is highly ionised. The salts are nearly all anhydrous like those of ammonium, potassium, rubidium, caesium and silver. The thallous halides are usually lower melting than the alkali halides. Resembalance to silver is particularly shown by the very slight solubility of the chloride, bromide and iodide and high solubility of the fluoride. But unlike silver, thallous chloride does not form a soluble ammine complex.

16.2. COMPARISON OF BORON AND SILICON: DIAGONAL RELATIONSHIP

The charge/radius ratios for boron and silicon are 15 and 10 indicating closeness in their behaviour although they are members of different groups of the Periodic Table.

Element	B	Si
Charge on the ion	+3	+4
Ionic Radius (A)	0.2	0.39
Charge/radius	15	10

The considerably high value for silicon must be taken as a suggestion that the chemistry of silicon will be dominated by covalence. The main points of resemblances between boron and silicon are the following:

1. The hydroxides of boron and silicon are weak but definite acids, H_3BO_3

and H_4SiO_4 (K^I_A, $H_3BO_3 = 6 \times 10^{-10}$; K^I_A, $H_4SiO_4 = \sim 10^{-10}$). These do not show any basic properties.

2. Boric acid reacts with alcohols in presence of H_2SO_4 to form alkyl or aryl borates, $B(OR)_3$. Orthosilicic acid also forms a series of volatile esters, $Si(OR)_4$.

3. Halides of both boron and silicon are readily hydrolysed to boric acid and silicic acid.

4. Both boron and silicon form volatile hydrides, both being obtained by a common method of acid hydrolysis of magnesium boride and magnesium silicide. Due to electron deficient character, the boron hydrides have unique hydrogen bridge bond, which is not necessary for the silicon hydrides.

5. Both B_2O_3 and SiO_2, being acidic oxides, are capable of reacting with basic oxides to form metal borates and metal silicates.

16.3. COMPOUNDS OF THE GROUP IIIB ELEMENTS

16.3.1. Boron Hydrides (Boranes) and Borohydrides (Tetrahydroborates):

Boron Hydrides: Stock's original method of synthesis involved acid hydrolysis of metal borides like Mg_3B_2. By this procedure a mixture of B_5H_{10}, B_6H_9, B_6H_{10} and $B_{10}H_{14}$ was obtained. No B_2H_6 could be obtained by this procedure as it was readily decomposed by water. Nowadays Stock's method is hardly used; instead, specialised methods are used for particular boron hydrides.

Diborane is best made by adding slowly a solution of BF_3 in dry ether to an etheral slurry of finely powdered $LiAlH_4$:

$$4BF_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 3LiF + 3AlF_3$$

The B_2H_6 alongwith the ether is passed through a cold condenser whereby the ether is retained, and then the B_2H_6 is collected in a trap cooled in liquid nitrogen. Diborane is also obtained by reacting a borohydride with sulphuric acid:

$$2NaBH_4 + H_2SO_4 \rightarrow B_2H_6 + Na_2SO_4 + 2H_2$$

Interaction of BCl_3 with H_2 over a Cu-Al catalyst at ~ 450°C also gives B_2H_6.

Pentaborane (B_5H_9) is obtained in good yield on heating a mixture of B_2H_6 and H_2 to ~250°C. B_2H_6 gives a moderate yield of B_5H_{11} at 115°C. B_5H_{11} and H_2 give at 100°C a mixture of B_2H_6 and B_4H_{10}.

All the boranes burn in air or oxygen, if ignition occurs, to give boric oxide and water:

$$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$$

Diborane reacts violently with halogens to form boron halides:

$$B_2H_6 + 6Cl_2 \rightarrow 2BCl_3 + 6HCl$$

Boron hydrides are hydrolysed by water to boric acid and hydrogen:

$$B_2H_6 + 6H_2O \rightarrow 2B(OH)_3 + 6H_2$$

With hydride ion B_2H_6 gives borohydrides.

Some Lewis bases break open the banana bond of B_2H_6 to give addition compounds:

$$B_2H_6 + 2R_3N \rightarrow 2(R_3N \rightarrow BH_3)$$
$$B_2H_6 + 2R_2NH \rightarrow 2(R_2NH \rightarrow BH_3)$$
$$B_2H_6 + 2PF_3 \rightarrow 2(F_3P \rightarrow BH_3)$$

The structure of boron hydrides has already been discussed (Chapter 13).

Borohydrides (*Tetrahydroborates*): The borohydrides contain the complex $[BH_4]^-$ ion. Sodium borohydride is formed out of the reaction of sodium hydride with boric ester at 250°C, and is extracted from the products with isopropylamine.

$$4NaH + B(OCH_3)_3 \rightarrow Na[BH_4] + 3NaOCH_3$$

Lithium borohydride is best obtained by the reaction of diborane with an ether solution of lithium hydride.

$$B_2H_6 + 2LiH \rightarrow 2Li[BH_4]$$

Sodium borohydride and lithium borohydrides are white crystalline non-volatile solid. Sodium borohydride may be recrystallised from aqueous solution but lithium borohydride is rapidly decomposed by water. Both are stable to heat upto ~275°C.

The borohydrides are readily decomposed by acids:

$$2NaBH_4 + H_2SO_4 \rightarrow B_2H_6 + 2H_2 + Na_2SO_4$$

The sensitivity of BH_4^- towards aqueous H^+ is due to the strong electron acceptor behaviour of H^+, which results in extraction of H^- from BH_4^- and liberation of H_2:

$$BH_4^- + H^+(H_2O) \rightarrow BH_3 + H_2 + (H_2O); 2BH_2 \rightarrow B_2H_6$$

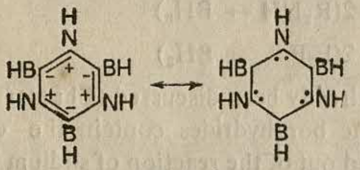
Like lithium aluminium hydride, the borohydride ion is also a formidable reducing agent, thus reducing carbonyl compounds to alcohols. The borohydride ion is tetrahedral and the crystal structure of the sodium salt has been found to be ionic being composed of face-centred cubic lattice of sodium and borohydride ions.

In the borohydride ion, $[BH_4]^-$, boron uses sp^3 hybridisation:

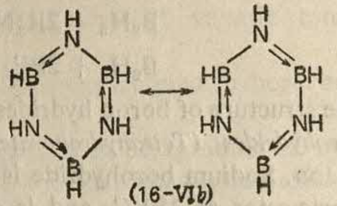
$$B \ \underset{2s}{\underline{\uparrow\downarrow}} \ \underset{2p}{\underline{\uparrow}} \ \underset{2p}{\underline{\ \ }} \ \underset{2p}{\underline{\ \ }} + 1 \text{ electron hybridises to } \underset{2(sp^3)}{\underline{\uparrow}} \ \underset{2(sp^3)}{\underline{\uparrow}} \ \underset{2(sp^3)}{\underline{\uparrow}} \ \underset{2(sp^3)}{\underline{\uparrow}}$$

The four tetrahedral hybrid orbitals overlap with 1*s* orbitals of four hydrogen atoms each containing one unpaired electron. Alternatively if we assume BH_4^- to be formed by the combination of BH_3 and H^- then there will be three usual covalent bonds between boron and three hydrogens, and a coordinate link from H^- to boron.

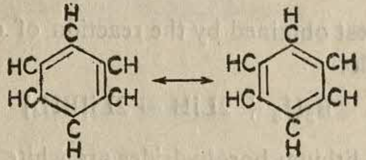
16.3.2. Borazole (Borazine) : The electron deficient character of boron is manifested in a number of compounds containing boron bound to N, P, S, etc, One such interesting compound is borazole (also called borazine) (16-VI), $B_3N_3H_6$, which has a resemblance with benzene (16-VII) in having two resonating structures containing alternate NH and BH groups. It is conveniently obtained by heating NH_4Cl and BCl_3, the product being chloroborazole, $B_3N_3H_3Cl_3$ (16-VIII). The chloroborazole is next reduced by sodium borohydride in ether:



(16-VIa)

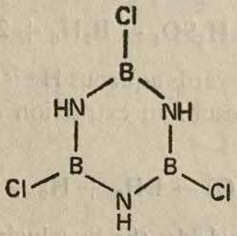


(16-VIb)



(16-VII)

$$3NH_4Cl + 3BCl_3 \xrightarrow[140-150°C]{C_6H_5Cl}$$



$$\xrightarrow[\text{eher}]{NaBH_4} B_3N_3H_6$$

(16-VIII)

Borazole has also been prepared by the pyrolysis of a boron-diammoniate in a sealed tube at ~200°C:

$$3B_2H_6.(NH_3)_2 \rightarrow 2B_3N_3H_6 + 12H_2$$

The so-called boron-diammoniate is obtained as a white solid by the reaction of diborane and ammonia. Its structure shows that it is really $[H_2B(NH_3)_2][BH_4]$.

In borazole the boron and the nitrogen atoms together are like the six carbon atoms in benzene. In benzene each carbon is sp^2 hybridised and is bonded to two carbons and one hydrogen. The remaining p_z orbital can overlap with another p_z orbital of a neighbouring carbon to make a double bond. Alternatively all the p_z orbitals of the six carbons may be assumed to overlap to form π-type M.O.'s. In borazole the three nitrogens and the three borons are sp^2 hybridised. Overlap

$$C\ \ \underset{2s}{\underline{\uparrow\downarrow}}\ \underset{2p}{\underline{\uparrow}}\ \underset{2p}{\underline{\uparrow}}\ \underset{2p_z}{\underline{\quad}}\ \ \text{hybridises to}\ \ \underset{2(sp^2)}{\underline{\uparrow}}\ \underset{2(sp^2)}{\underline{\uparrow}}\ \underset{2(sp^2)}{\underline{\uparrow}}\ \underset{2p_z}{\underline{\uparrow}}$$

$$\text{B}\ \underset{2s}{\underline{\uparrow\downarrow}}\ \underset{2p}{\underline{\uparrow}}\ \underset{2p}{\underline{\ \ }}\ \underset{2p_z}{\underline{\ \ }}\ \text{hybridises to}\ \underset{2(sp^2)}{\underline{\uparrow}}\ \underset{2(sp^2)}{\underline{\uparrow}}\ \underset{2(sp^2)}{\underline{\uparrow}}\ \underset{2p_z}{\underline{\ \ }}$$

$$\text{N}\ \underset{2s}{\underline{\uparrow\downarrow}}\ \underset{2p}{\underline{\uparrow}}\ \underset{2p}{\underline{\uparrow}}\ \underset{2p_z}{\underline{\uparrow}}\ \text{hybridises to}\ \underset{2(sp^2)}{\underline{\uparrow}}\ \underset{2(sp^2)}{\underline{\uparrow}}\ \underset{2(sp^2)}{\underline{\uparrow}}\ \underset{2p_z}{\underline{\uparrow\downarrow}}$$

of the sp^3 orbitals gives three covalent bonds to nitrogen and boron while overlap of the p_z orbitals provides a π-bond from nitrogen to boron (16-VIB). Resonance will lead to equivalent B-N distances. In effect a π-system comparable to that of benzene results. Many physical properties of borazole are similar to those of benzene:

	Borazole	Benzene
B-N distance	1.42A	—
C-C distance	—	1.41A
Molecular Weight	80.5	78
B. P. (°C)	53	80
Critical temperature	21.4	21.1
Heat of vaporisation (Kcal/mole)	7	7.4

Because of these similarities borazole has been nicknamed *inorganic benzene.* However borazole is more reactive than benzene, Unlike benzene, borazole undergoes addition reactions, say with HCl:

$$B_3N_3H_6 + HCl \rightarrow (-H_2N-BHCl-)_3$$

16.3.3. Boron Trifluoride, Fluoroboric Acid and Potassium Fluoroborate: Boron trifluoride is formed by the action of fluorine on boron. It is also obtained by heating a mixture of calcium fluoride, boron trioxide and concentrated sulphuric acid:

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 \rightarrow 2BF_3 + 3CaSO_4 + 3H_2O$$

The gas reacts with water to form boric acid and *fluoroboric acid:*

$$4BF_3 + 3H_2O \rightarrow H_3BO_3 + 3HBF_4$$

Fluoroboric acid is also obtained by dissolving boric acid in cooled 50% HF:

$$H_3BO_3 + 4HF \rightarrow HBF_4 + 3H_2O$$

Addition of potassium salts to HBF_4 precipitates potassium fluoroborate. The fluoroborate is tetrahedral (sp^3 hybridisation) and is isomorphous with $KClO_4$.

Boron trifluoride forms a number of stable addition compounds with Lewis bases. Some reactions are shown below:

$$BF_3 + NR_3 \rightarrow F_3B \leftarrow NR_3$$

$$BF_3 + R_2O \rightarrow F_3B \leftarrow OR_2$$

$$BF_3 + 3NaBH_4 \rightarrow 2B_2H_6 + 3NaF$$

$$2BF_3 + 6RMgX \rightarrow 2R_3B + 3MgF_2 + 3MgX_2$$

16.3.4. Boron Trichloride : It is obtained by burning boron in chlorine, by heating B_2O_3 with PCl_5 in a sealed tube or by passing dry chlorine gas over a heated mixture of B_2O_3 and carbon. It is first condensed in a freezing mixture and then purified from chlorine by distillation over mercury.

$$B_2O_3 + 3PCl_5 \rightarrow 2BCl_3 + 3POCl_3$$

$$B_2O_3 + 3C + 3Cl_2 \rightarrow 2BCl_3 + 3CO$$

Some typical reactions of BCl_3 are given below:

$$BCl_3 + 3NH_3 \rightarrow B(NH_2)_3 + 3HCl$$

$$BCl_3 + 3ROH \rightarrow B(OR)_3 + 3HCl$$

$$BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl$$

$$2BCl_3 + 6RMgX \rightarrow 2R_3B + 3MgCl_2 + 3MgX_2$$

16.3.5. Boron Nitride : This is prepared by heating borax with NH_4Cl, extracting with HCl, and washing:

$$Na_2B_4O_7 + 2NH_4Cl \rightarrow 2NaCl + 2BN + B_2O_3 + 4H_2O$$

This forms an infusible powder and is not attacked by dilute acid and dilute alkali. It is structurally related to diamond and graphite (Chapter 17).

16.3.6. Borax : Borax is sodium tetraborate decahydrate, $Na_2B_4O_7.10H_2O$. This is mostly obtained from its natural source in California. Another tetraborate mineral is *kernite* $Na_2B_4O_7.4H_2O$. *Colemanite* $Ca_2B_6O_{11}.5H_2O$, a hexaborate, is also an important source of borax. When sodium tetraborate is crystallised from a hot solution above 60°C a pentahydrate separates and below 60°C the decahydrate, borax, crystallises. Colemanite, on boiling with sodium carbonate and on crystallising the filtrate below 60°C also gives good quality borax:

$$Ca_2B_6O_{11} + 2Na_2CO_3 \rightarrow Na_2B_4O_7 + 2NaBO_2 + 2CaCO_3$$

Borax gives a slightly alkaline reaction in aqueous solution because of hydrolysis, boric acid being only a weak acid:

$$Na_2B_4O_7 + 3H_2O \rightarrow 2NaBO_2 + 2H_3BO_3$$

On heating borax first swells due to forming anhydrous borax which then changes to metaborate and boron trioxide:

$$Na_2B_4O_7 \rightarrow 2NaBO_2 + B_2O_3$$

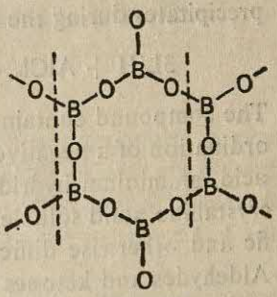
Fused borax can dissolve metal oxides to yield clear glasses of characteristic colours:

$$Na_2B_4O_7 + CuO \rightarrow 2NaBO_2 + Cu(BO_2)_2 \text{ (green)}$$

$$Na_2B_4O_7 + CoO \rightarrow 2NaBO_2 + Co(BO_2)_2 \text{ (blue)}$$

Such reactions form the basis of *borax-bead tests*. Borax and other metal borates are all cyclic or linear polymers formed by the sharing of oxygen atoms by BO_3 or BO_4 units. The structure of borax ion is represented as (16-IX):

Borax finds extensive use in making optical and hard glass, as an antiseptic, in the manufacture of enamels, and as a preservative. Because of low solubility of calcuim and magnesium borates, borax is also used as a water softener.


(16-IX)

16.3.7. Boric Acid : Boric acid is obtained in the form of scales by boiling borax with acids and then crystallising. The acid is also produced during hydrolysis of boron halides:

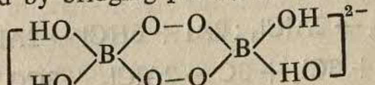
$$Na_2B_4O_7 + 2HCl + 5H_2O \rightarrow 2NaCl + 4H_3BO_3$$

$$BCl_3 + 3H_2O \rightarrow H_3BO_3 + 3HCl$$

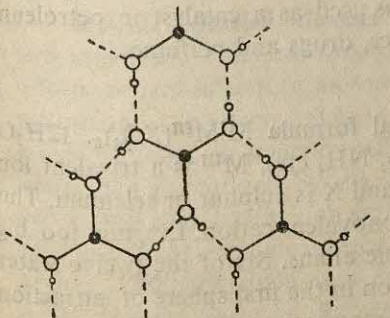
The acid has distinct volatility and can be removed with repeated evaporation with HCl. Around 100°C the acid is changed to metaboric acid (HBO_2), at 140°C to pyroboric acid ($H_2B_4O_7$) and finally at higher temperature to B_2O_3. With alcohols (in presence of sulphuric acid) alkyl borates are formed, this being the basis of detecting borates and boric acid in qualitative analysis.

$$H_3BO_3 + 3C_2H_5OH \rightarrow B(OC_2H_5)_3 + 3H_2O$$

The esters burn in air with a green flame. On fusion with metal oxides coloured borate glasses are formed. On fusion with NH_4HF_2 ultimately BF_3 is obtained. Treatment of boric acid with sodium peroxide provides sodium peroxyborate which is now known to have the structure of $[B_2(O_2)_2(OH)_4]^{2-}$ in which two tetrahedral borons are linked by bridging peroxy groups (16-X).


(16-X)

Crystal structure of boric acid shows a layer structure of $B(OH)_3$, the different $B(OH)_3$ being held strongly by hydrogen bonding. The layers in the crystal are ~3.2A apart being held by van der Waal's forces (16-XI):


O=oxygen; ●=boron; o=hydrogen
(16-XI)

Conductance of aqueous solution of otherwise weak boric acid is enhanced by the addition of polyhydric alcohol, such as mannitol, glycerol etc. The strength of boric acid is thereby so much increased that it becomes possible to titrate the solution with an alkali using phenolphthalein as an indicator (section 16.1.2). This reaction is also the basis of the borax-phenolphthalein test of glycerol.

16.3.8. Lithium Aluminium Hydride : Aluminium chloride reacts in dry ether with lithium hydride to produce lithium aluminium hydride. First aluminium hydride is formed which reacts with excess lithium hydride. Lithium chloride precipitates during the reaction.

$$3LiH + AlCl_3 \rightarrow AlH_3 + 3LiCl\ ;\ LiH + AlH_3 \rightarrow Li[AlH_4]$$

The compound contains the complex hydride anion $[AlH_4]^-$ formed by the co-ordination of a negative hydride from the lithium hydride molecule to the Lewis acid, aluminium hydride. This is a celebrated reducing agent. It is non-volatile, crystalline solid soluble in many organic solvents. It can bring about many specific and otherwise difficult reductions such as that of $-COOH$ to $-CH_2OH$. Aldehydes and ketones are reduced to alcohols. Nitriles are reduced to primary amines and hydrocarbon halides to the corresponding hydrocarbons without destroying any unsaturation that may be present in the molecule. With strong donors such as pyridine $Li[Al(py)_4]$ is formed.

(*a*) $$4CH_3COOH + 3LiAlH_4 \rightarrow LiAl(CH_3CH_2O)_4 + 2LiAlO_2 + 4H_2$$
$$LiAl(CH_3CH_2O)_4 + 4H_2O \rightarrow 4CH_3CH_2OH + LiOH + Al(OH)_3$$

(*b*) $$2CH_3CN + LiAlH_4 \rightarrow LiAl(CH_3CH_2N)_2$$
$$LiAl(CH_3CH_2N)_2 + 4H_2O \rightarrow CH_3CH_2NH_2 + LiOH + Al(OH)_3$$

(*c*) $$4CH_2 = CH\text{-}CH_2Br + LiAlH_4 \rightarrow 4CH_2 = CH\text{-}CH_3 + LiAlBr_4$$

16.3.9. Anhydrous Aluminium Chloride : This is prepared by heating aluminium in chlorine or HCl, or by heating a mixture of alumina and carbon in a current of dry chlorine:

$$2Al + 3Cl_2 \rightarrow 2AlCl_3\ ;\ 2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$$
$$Al_2O_3 + 3Cl_2 + 3C \rightarrow 2AlCl_3 + 3CO$$

Crude $AlCl_3$ is also obtained by passing chlorine over a heated mixture of bauxite and carbon. This is a white hygroscopic material. It rapidly absorbs moisture and forms the hexahydrate. Vapour density measurements at ~350°C indicates a dimeric chlorine bridged structure Al_2Cl_6. It is used as a catalyst in petroleum cracking, in Friedel Crafts reaction and in dyes, drugs and perfumes.

16.3.10. Alums : Alums have the general formula $M^IM^{III}(XO_4)_2 . 12H_2O$ where M^I is a monovalent ion (Na, K, Rb, Cs, NH_4 etc), M^{III} is a trivalent ion (Al, Fe, Cr, Mn, Ir, Ga, In, Tl, V, Co, Rh) and X is sulphur or selenium. The size factors are such that neither too small a monovalent cation, Li^+, nor too big a trivalent ion like the lanthanides forms stable alums. Six of the twelve water molecules are coordinated to the trivalent cation in the first sphere of attraction and the other six water molecules surround the monovalent cation. The arrangement of $[M^I(H_2O)_6]^+$, $[M^{III}(H_2O)_6]^{3+}$ and SO_4^{2-} groups is not always the same.

Potash alum is usually obtained by roasting *alumstone* $K_2SO_4.3Al_2SO_4(OH)_4$ in air and crystallising from water:

$$\begin{array}{c} K_2SO_4.3Al_2SO_4(OH)_4 \rightarrow K_2SO_4.Al_2(SO_4)_3 + 2Al_2O_3 + 6H_2O \\ \downarrow \text{water} \\ KAl(SO_4)_2.12H_2O \end{array}$$

Ammonium aluminium alum can be made by the addition of ammonium sulphate to aluminium sulphate in aqueous medium and crystallising. Alums are dissociated completely into ions in aqueous medium and therefore they cannot be regarded as complex entities in aqueous solution. They respond to the usual tests of aquo metal ions.

Aluminium alums are chiefly used in dyeing as a mordant. There are numerous dyes whose molecules, although they adhere readily to fibres of animal origin such as silk or wool, do not attach firmly to vegetable fibres such as cotton. However, if cotton is first soaked in a solution of ammonium alum (or any Al^{3+} solution) and then treated to precipitate aluminium hydroxide, many of these dyes are adsorbed on the aluminium oxide and hence are strongly held in the cloth. Common mordants include salts of Al, Fe. Aluminium alums also find use in purification of water for human consumption. Water is treated with alum and then made basic with sodium carbonate. Aluminium hydroxide precipitates and this carries down with it suspended foreign matter including many microorganisms. The water is finally treated with chlorine, iodine or in some cases with ozone.

16.3.11. Alundum : This is a basic refractory material obtained by fusing bauxite in an electric arc furnace and allowing the impurities to settle down. Impure red bauxite (containing Fe_2O_3 as impurity) is first treated with NaOH solution. The Fe_2O_3 is filtered off and the filtrate is diluted with sufficient water to precipitate pure $Al(OH)_3$. This is dried and fused at about 2000°C in the electric furnace. If the bauxite contains some Fe_2O_3 and silica it is mixed with fine coke and the mixture fused. The coke reduces the impurities and a heavy iron-silicon alloy is formed. The alloy sinks below the fused alumina. Finally the entire mass is cooled and the solidified alumina i.e. alundum is taken out.

16.3.12. Activated Alumina : Aluminium oxide, Al_2O_3, may attain at least two important structural forms, one called α-Al_2O_3 and the other γ-Al_2O_3. The α-form occurs in nature as *corundum* which is resistant to water and acids. As against this the γ-form takes up water and dissolves in acids. This form has a non-stoichiometric structure (Chapter 19), that is, it has lesser number of aluminium than is required by the formula. The γ-form is therefore distorted, less dense, soft and has a high surface area. These qualities make γ-alumina an excellent reagent for dehydration, decolourisation and for adsorption chromatography. Ordinary aluminium hydroxide when dehydrated at ~400°C becomes *active alumina* (γ-form). Remember raising the temperature to ~1000°C will convert γ-alumina to α-alumina destroying all its excellent adsorption properties.

16.3.13. Gallium (III) Chloride: It is made by heating gallium in an atmosphere of chlorine or HCl gas. It can be purified by distillation in an atmosphere of nitrogen. It forms long white needles (B.P. ~ 201°C) which fume in moist air due to formation of HCl through hydrolysis. It is very soluble in ether and is dimeric below 600°C. Its aqueous solution readily deposits the hydroxide. It is a more efficient catalyst than $AlCl_3$ for some hydrocarbon syntheses.

16.3.14. Gallium (III) Sulphate : This can be crystallised as $Ga_2(SO_4)_3.18H_2O$ from a dilute sulphuric acid solution of the freshly precipitated hydroxide. Like aluminium (III) it forms ammonium alum $NH_4Ga(SO_4)_2.12H_2O$.

16.3.15. Indium (III) Chloride : It can be obtained by heating the metal in chlorine or a mixture of the metal oxide and carbon in chlorine. It forms white leaflets. It has a strong trend to form hexachloro complexes in presence of chloride ions eg. $K_3[InCl_6]$.

16.3.16. Indium (III) Sulphate : This is obtained by dissolving indium oxide or hydroxide in dilute H_2SO_4, concentrating and crystallising. Alum type double sulphates with NH_4^+, Rb^+ and Cs^+ are formed below 35°C.

16.3.17. Thallium (III) Chloride : Oxidation of thallium (I) chloride with chlorine in aqueous medium gives a solution which can be concentrated in a current of chlorine to colourless crystals of $TlCl_3.4H_2O$. A dilute aqueous solution hydrolyses to insoluble brown thallium (III) oxide, $Tl_2O_3.H_2O$. Thallium (III) chloride readily forms chloro complexes $M^I_3[TlCl_6]$.

16.3.18. Thallium (I) Chloride : Thallium metal dissolves in nitric acid and from this solution $TlNO_3$ crystallises. The thallium (I) chloride is precipitated as a curdy white substance when chloride ions are added to a solution of the nitrate or any other soluble salts. Dry chlorine converts it to $TlCl_3$.

16.3.19. Thallium (I) Sulphate : The compound Tl_2SO_4 crystallises in large colourless prisms on dissolving thallium metal in dilute sulphuric acid. The sulphate is isomorphous with potassium, rubidium and caesium sulphates. It forms an alum with aluminium sulphate $TlAl(SO_4)_2.12H_2O$.

16.4. GOLDSCHMIDT'S ALUMINO THERMIT PROCESS

Aluminium can displace less electropositive metals (standard potentials above −1.6 volts) from their oxides at high temperature. The potential of Al^{3+}/Al couple is −1.66 volts. Carbon-free metals can be produced by reducing metal oxides by aluminium powder. Such reductions have been done for oxides of chromium ($E°$, $Cr^{3+}/Cr = -0.74$ volts), manganese ($Mn^{2+}/Mn = -1.18$ volts), nickel ($Ni^{2+}/Ni = -0.25$ volts), iron, etc as also for the oxides of boron and silicon. The reduction reactions are very exothermic so that the reduced metal is obtained in a fused state. The exothermicity has been utilised in thermite welding of steel. The broken parts of steel are placed in position, are surrounded by a mould of clay and heated to redness. The *thermite*, a mixture of powdered aluminium and ferric oxide, is taken in a crucible provided with a tapping hole, and the mixture ignited by means of a fuse of magnesium ribbon inserted into powdered magnesium and barium peroxide mixture. Ferric oxide gets reduced and the molten iron drops into the broken parts of red hot steel making a good welding.

16.5. ISOLATION OF THE GROUP IIIB ELEMENTS

16.5.1. Boron : It occurs in nature as *boric acid* (H_3BO_3), *borax* ($Na_2B_4O_7$, $10H_2O$), *colemanite* ($Ca_2B_6O_{11}.5H_2O$) *kernite* ($Na_2B_4O_7.4H_2O$) etc. The element can be obtained by the reduction of the oxide. Ignition of boric acid gives B_2O_3 which is reduced by excess magnesium at a high temperature:

$$B_2O_3 + 3Mg \rightarrow 2B + 3MgO$$

The product is contaminated with magnesium boride, Mg_3B_2, and is purified by boiling with dilute HCl. Hydrogen reduction of BCl_3 or BBr_3 provides 99% pure boron. Boron thus obtained is a brown, amorphous powder. Black, crystalline boron has been prepared by reducing BBr_3 vapour with hydrogen at 1300°C on a tantalum filament.

Pure boron has also been obtained by electrolysis of (*a*) KBF_4 in fused KCl and (*b*) fused mixture of KBF_4, KCl and B_2O_3. A graphite-lined pot of some heat-resistant alloy serves as the anode into which is lowered an iron cylinder serving as the cathode. The anode and the cathode are kept cool by circulating cold water through them. For KCl-KBF_4 system chlorine is evolved at the anode while the liberated potassium reacts with KBF_4 releasing pure boron on the cathode:

$$K^+ + e \rightarrow K\ ;\ 3K + KBF_4 \rightarrow 4KF + B$$

For KCl-KBF_4-B_2O_3 system oxygen is evolved at the anode and boron at the cathode. Effectively B_2O_3 is electrolysed.

16.5.2. Aluminium : Aluminium is present in the earth's crust in many different forms: as silicates (*felspar*, $K_2O.Al_2O_3.6SiO_2$; *kaolin* (*clay*), $Al_2O_3.2SiO_2.2H_2O$), as oxides (*bauxite*, $Al_2O_3.2H_2O$), as *cryolite* (Na_3AlF_6), as *alunite* or *alumstone* ($K_2SO_4.3Al_2(SO_4)(OH)_4$), etc.

Electrolytic production of aluminium was a big problem to chemists and chemical engineers. The commonest source was Al_2O_3 but it melted only at 2050°C. Suitable materials for the construction of an electrolytic cell to be operated above 2050°C were not readily available. Furthermore radiation losses would be too great. The need was to find a suitable salt which would fuse at a reasonable temperature, would dissolve Al_2O_3 and allow the electrolysis to continue. Two young men, Hall and Heroult, discovered that fused cryolite,

Na_3AlF_6, was the right solvent. Greenland is the only source of natural cryolite but it is usually prepared artificially by reacting Na_2O, Al_2O_3 and HF:

$$3Na_2O + Al_2O_3 + 12HF \rightarrow 2(AlF_3.3NaF) + 6H_2O$$

For the purpose of extraction bauxite is by far the best source. Purification of aluminium being quite difficult natural bauxite is treated to obtain pure alumina. Bauxite, contaminated by silicates and iron oxide, is finely ground and digested with sodium hydroxide solution under pressure at moderate temperature. Since aluminium oxide is amphoteric it dissolves to form sodium aluminate, while ferric oxide, clay and other impurities are left behind. Silica dissolves slightly but is precipitated, during digestion, as sodium aluminium silicate. Filtered sodium aluminate solution is diluted to precipitate hydrated aluminium oxide, which is collected and ignited to get anhydrous Al_2O_3. Aluminium is then recovered by an electrolytic procedure. Cryolite, Na_3AlF_6, or an artificial mixture of 3 NaF and 1 AlF_3 is fused and purified Al_2O_3 added to make $\sim 5\%$ solution in cryolite. This electrolyte is now charged into a cell made up of large steel boxes lined with a layer of refractory material and an inner lining of carbon. The carbon lining serves as the cathode and some carbon rods hanging into the electrolyte serve as the anode. Aluminium oxide in fused cryolite dissociates into Al^{3+} and O^{2-} ions. During electrolysis the following reactions occur:

$$\text{at the cathode: } Al^{3+} + 3e \rightarrow Al$$

$$\text{at the anode: } O^{2-} \rightarrow \tfrac{1}{2}O_2 + 2e;\ C + \tfrac{1}{2}O_2 \rightarrow CO;\ C + O_2 \rightarrow CO_2$$

Temperature of the electrolyte is maintained above the melting point of aluminium ($> 660°C$) so that the metal collects in fused state at the bottom of the cell and is removed from time to time through a tap hole. The purity reached is $> 99\%$. The price of many of our commercial products is dictated by the cost of production. In USA in 1850's aluminium used to be prepared by the sodium reduction of $AlCl_3$. The cost of aluminium in 1850's was 550 dollars per pound, being dependent on the high cost of sodium. With cheaper electrolytic processes of manufacture of sodium the price of aluminium fell to 8 dollars per pound in 1886. Then (1886) a young American, Hall, and a young French, Heroult, both twenty two years old indepentently published within a span of three months their method of aluminium production from bauxite. And thus the price of aluminium went down to only ~ 15 cents per pound in 1940's.

Processes have also been developed to extract aluminium from clay. In the Buchner process the clay is heated under pressure with HNO_3 in autoclaves. Al_2O_3 passes into solution as nitrate leaving behind SiO_2, Fe_2O_3, Ti_2O_3 etc. The solution contains alkali and alkaline earth nitrates. The aluminium nitrate is separated by fractional crystallisation, and is then ignited to Al_2O_3. The Al_2O_3 is then worked up electrolytically to yield aluminium. In the Haguland process the clay is heated with coke and iron pyrites in an electric furnace. A slag consisting of 80% Al_2O_3 and 20% Al_2S_3 floats up. The slag is removed and treated with HCl when the sulphide decomposes to $AlCl_3$ and H_2S but the Al_2O_3 remains undissolved. The oxide is then worked as described above for aluminium extraction from bauxite.

Although aluminium has a negative standard potential it is not easily attacked by water or dilute weak acids. This is because of the formation of an insoluble aluminium hydroxide coating which prevents further action by water or weak acids. If the aluminium is rubbed with mercury the metal is amalgamated and the formation of the insoluble hydroxide is prevented. Apparently mercury interferes with the adhesion of $Al(OH)_3$ coating to the surface of aluminium. Hence amalgamated aluminium reacts better with water or weak acids. However aluminium reacts rapidly with an alkaline solution because the aluminium hydroxide dissolves in alkali to form aluminate.

16.5.3. Gallium, Indium and Thallium : The three elements accompany zinc blende and pyrites ores in very small quantities. The extraction procedure is very much dependent on the quality of the ore.

Gallium: Zinc blende is treated with a deficient amount of aqua regia. The filtered solution is treated with metallic zinc when less electropositive elements such as Hg, Ag, Cd, Cu are precipitated. The solution is then filtered and then boiled with further quantities of zinc. Basic salts of zinc, gallium, iron and chromium and also alumina and silica are precipitated. The precipitate is dissolved in HCl and neutralised with ammonia. Zinc and gallium are now precipitated as sulphides by H_2S. The sulphides are dissolved in dilute HCl and treated with sodium carbonate. The basic carbonate is converted to sulphate and the solution electrolysed to get the metal. A second method of extraction is indicated in outline in Chart 16-I.

Indium: Zinc blende rich in indium is treated with deficient quantity of HCl which takes most of the more basic elements in solution. Further treatment with HCl brings indium and other heavy metals into solution. The heavy metals are now precipitated by H_2S in acid solution. The solution is next oxidised by HNO_3 and indium is precipitated in presence of NH_4Cl as hydrated oxide alongwith iron (III) oxide hydrate. The precipitate is dissolved in little HCl and iron (III) reduced by SO_2. The solution is then treated with $BaCO_3$ to precipitate indium as hydrated oxide. Alternatively the HCl solution may be treated with thiocyanate and iron thiocyanate extracted with ether. The aqueous solution is then treated with ammonia whereby indium precipitates. Finally the metal is obtained by reduction of the oxide by hydrogen or by electrodeposition of a salt.

Electrodeposition has been done from a number of electrolytes, namely sulphates and fluoroborates. pH ~ 2.0 and temperature of ~ 20-35°C are used. Anode consists of crude indium while the cathode is pure indium.

Thallium: Some zinc blende or pyrites often carry significant amount of thallium. During roasting of these ores the thallium is carried in the flue dust, probably as thallous sulphate. The flue dust is leached with water and the thallium (I) is precipitated as chloride by the addition of HCl. It is purified by reconversion to the sulphate and by reprecipitation as the chloride. Finally thallium is electrodeposited on the cathode by electrolysis of a sulphuric acid solution.

A platinum anode and a platinum, nickel or stainless steel cathode are used in the electrolysis. Metallic thallium has also been precipitated from a thallous solution by zinc. Commercial thallium generally carries lead as impurity. The lead can, however, be removed by passing H_2S into a weakly acid solution of the metal.

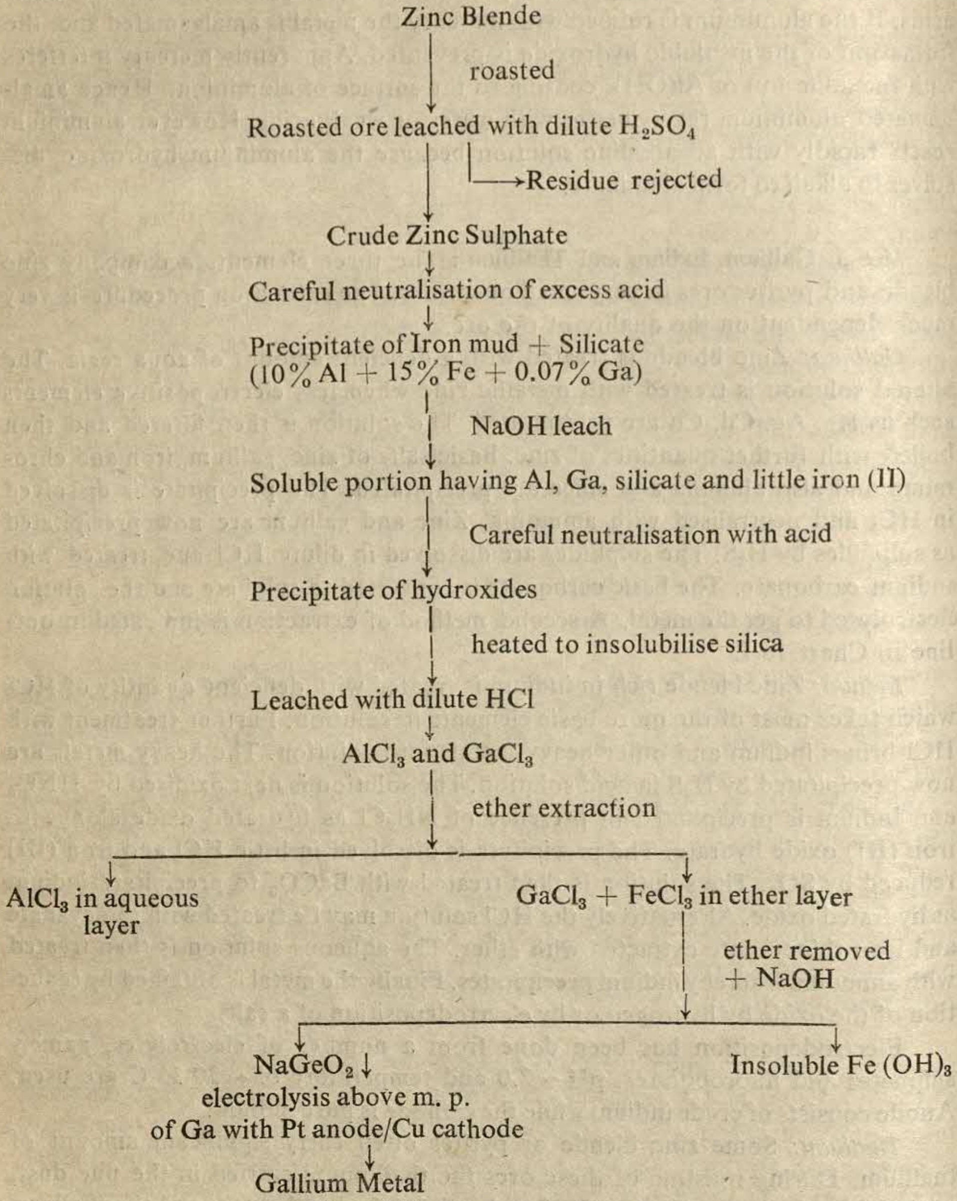

Zinc Blende
roasted
Roasted ore leached with dilute H_2SO_4
Residue rejected
Crude Zinc Sulphate
Careful neutralisation of excess acid
Precipitate of Iron mud + Silicate
(10% Al + 15% Fe + 0.07% Ga)
NaOH leach
Soluble portion having Al, Ga, silicate and little iron (II)
Careful neutralisation with acid
Precipitate of hydroxides
heated to insolubilise silica
Leached with dilute HCl
$AlCl_3$ and $GaCl_3$
ether extraction
$AlCl_3$ in aqueous layer
$GaCl_3 + FeCl_3$ in ether layer
ether removed + NaOH
$NaGeO_2$ ↓
Insoluble $Fe(OH)_3$
electrolysis above m. p. of Ga with Pt anode/Cu cathode
Gallium Metal

Chart 16-I. Extraction of gallium

16.6. USES OF THE GROUP IIIB ELEMENTS

Aluminium and its alloys find important uses due to the lightness of the metal and its strength and toughness. The most important of the alloys is *duralumin*

(Cu 3.5–4.5%; Mg 0.3–1.0%; Mn 0.4–1.0%; Si 0.3–1.0% and Al, 92.5–95.5% *Aluminium bronze* is an alloy of copper (90%) and aluminium (~ 10%) with trace amounts of iron and other metals. Aluminium and its alloys are the major construction materials of the aircraft and other transportation industries. These are also used in corrugated roofing, collapsible tubes for pastes, decorative coatings and as a wrapping material in food industry.

Anodising: Because of the comparative corrosion resistance properties of aluminium, anodising of aluminium articles for decorative purposes has become very popular nowadays. Aluminium and its alloys may be given pleasingly coloured protective coatings by an electrolytic process. The cleaned aluminium object is made the anode in an electrolytic bath containing salts of one or more of copper, tin, cobalt, nickel, chromium, iron, silver, etc. Sometimes molybdates and tungstates are also used to achieve the desired colour and polish. On the passage of electric current oxygen is liberated at the anode and a fine decorative layer of aluminium oxide alongwith oxides of one or more of the above chosen transition metals is deposited on the aluminium article. These anodised aluminium articles are extremely pleasing to look at and have a long lasting lustre.

Gallium finds some use as a thermometric liquid for high temperature measurements.

16.7. ANALYTICAL REACTIONS OF THE GROUP IIIB ELEMENTS

Boron compounds are usually detected by the green colouration of a Bunsen flame, caused by a volatile alkyl borate ester. Free boric acid and alcohol react in presence of sulphuric acid to produce the ester:

$$B(OH)_3 + 3CH_3OH \rightleftharpoons B(OCH_3)_3 + 3H_2O$$

The sulphuric acid serves to shift the equilibrium to the right by taking up the water. In the case of an insoluble borate, it is mixed with CaF_2, H_2SO_4 and alcohol, and then held in the flame. Volatile BF_3 is formed, and gives a green flame:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF; M_2B_4O_7 + H_2SO_4 \rightarrow 2B_2O_3 + M_2SO_4 + H_2O$$

$$B_2O_3 + 6HF \rightarrow 2BF_3 + 2H_2O$$

The titrimetric determination of boric acid involves complexation with mannitol, glycerol, etc. when a strong monobasic acid is formed, which can be titrated with a standard alkali to a phenolphthalein endpoint.

Boric acid has to be removed by repeated heating with HCl before passing onto the detection of metal ions in group III and later qualitative groups.

Borax-beads play important role in detection of some metal ions. Fused borax dissolves some metallic oxides giving typical colours eg: $Na_2B_4O_7 + CuO \rightarrow Cu(BO_2)_2 + 2NaBO_2$: The metal oxide and the colour of the corresponding metaborate are: CuO, *blue*; Cu_2O, *red*; Cr_2O_3, *green;* MnO_2, *violet*, CoO, *deep blue;* FeO, *green*; Fe_2O_3, *brown*.

Aluminium accompanies iron (III) and chromium (III) in group IIIA of the qualitative scheme of analysis. The hydroxide of aluminium (III) dissolves in excess alkali to form aluminate. For quantitative estimation the metal is precipitated as hydroxide by NH_4OH and the precipitate ignited to Al_2O_3 and weighed.

Aluminium can also be precipitated as the pale yellow oxinate [Al(oxin)$_3$], from a weakly ammoniacal solution and weighed. The precipitate may also be dissolved in acid and the oxine content and hence the aluminium determined by a bromometric procedure (compare magnesium).

The acid solution of [Al(oxin)$_3$] is treated with excess KBr and the solution titrated with a standard $KBrO_3$ solution in the presence of methyl orange as indicator. 5, 7-dibromooxine is formed according to:

$$C_9H_7ON + 2Br_2 \rightarrow C_9H_5ONBr_2 + 2H^+ + 2Br^-$$

[Al(oxin)$_3$] will thus consume 12 bromine atoms which are generated by the reaction:

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

The end point is given by the discharge of the indicator colour due to oxidation by bromine. Since equivalent weight of $KBrO_3$ is one-sixth its molecular weight and since 1 Al $\equiv$ 12 Br we have:

$$1000 \text{ ml } N \text{ KBrO}_3 \equiv \tfrac{1}{12} \times 26.98 \text{ gm. Al}$$

$$\therefore 1 \text{ ml } N \text{ KBrO}_3 \equiv 0.002249 \text{ gm. Al}$$

Gallium, indium and *thallium* are precipitated with ammonia, and the precipitates ignited to the oxides and weighed. Thallium can also be estimated gravimetrically as thallous chromate. In qualitative scheme of analysis thallium (I) follows silver and mercurous mercury in group I. It gives an insoluble chloride, which unlike silver chloride is not soluble in ammonia.

STUDY QUESTIONS

1. Boron halides are Lewis acids but not Lewis bases. Comment.

2. Enumerate some points of boron chemistry where the electron deficient character of boron dictates the chemistry.

3. Distinguish between hydrogen bond and hydrogen bridge bond. Where do we expect such bonds to operate ?

4. A bivalent gallium compound, $GaCl_2$, can also be formulated as Ga[$GaCl_4$]. What experiments would distinguish between the two alternatives?

5. The differences in radii between Be^{2+} and B^{3+} and between Mg^{2+} and Al^{3+} are in each case 0.1A. But the differences in the radii of Ca^{2+} and Ga^{3+} and of Sr^{2+} and In^{3+} are above 0.3A. Comment (compare Chapter 4).

6. Outline the principles involved in the extraction of aluminium from bauxite, and clay.

7. Cite two boron compounds where two hybridisation schemes are used.

8. Give an account of the syntheses, structures and uses of sodium borohydride and lithium aluminium hydride.

9. Discuss the diagonal relationship between Be and Al.

10. Write short accounts of: (*a*) boric acid, (*b*) Goldschmidt's alumino thermit process, (*c*) activated alumina, (*d*) peroxyborate and (*e*) diborane.

11. Trivalent boron and quadrivalent silicon may both be viewed as electron deficient because while boron has a vacant 2*p* orbital silicon has vacant 3*d* orbital. Discuss.

12. Complexation is responsible for the alkalimetric determination of boric acid in presence of glycerol. Elucidate.

13. Wherever boron is four coordinate, the compounds conform to a tetrahedral geometry. Why the compounds are not square planar ?

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17

Group IVB. Carbon, Silicon, Germanium, Tin and Lead

This group includes carbon, silicon, germanium, tin and lead. Carbon is an essential ingredient of all living organism, and carbon compounds play crucial roles in vegetable and animal kingdom. The carbon dioxide and moisture of our atmosphere are worked up by plants through the agency of their green pigment, *chlorophyl,* and in the presence of sunlight into carbohydrates $(C_6H_{10}O_5)x$ (starch and cellulose). Carbohydrates are then consumed by the vegetable and animal kingdom and transformed into CO_2 and water. Thus CO_2 is fed back into the cycle. Carbon is found in nature as CO_2, as metal carbonates, as decay product of primeval vegetation in nature (eg. coal), and also as a decay product of primeval living organism (eg. petroleum). Silicon is the second commonest element of the earth's crust after oxygen and occurs in nature in abundant quantities as various silicate minerals and also as silica. The per cent abundances are: C(0.08%); Si(27.7%); Ge($\sim 10^{-11}$%); Sn($\sim 10^{-6}$%); Pb($\sim 10^{-5}$%)

17.1. COMPARATIVE STUDY OF THE GROUP IVB ELEMENTS

17.1.1. General Considerations : The chemistry of group IVB elements follows from their electronic configurations although the differences in properties between carbon and silicon are rather wide. All the elements have an outermost quantum shell composition of s^2p^2 although germanium, tin and lead have underneath these electrons a *d* or *f* subshell. The inner shells of carbon and silicon are those of the preceding noble gases (Table 17.1).

The four ionisation potentials (Table-17.1) taken together are exhorbitantly high. Just as in group IIIB the fall of the ionisation potentials along the group is not prominent. This appears to be a consequence of the enhanced deformation of non-noble gas structures of the inner shells. No compound is known in this group with a + 4 cation. Instead of attaining a noble gas or a pseudo noble gas configuration through a M^{4+} cation the elements attain the desired configurations in most cases with four single covalent bonds. The four covalent bonds are equivalent, tetrahedral and result from sp^3 hybridisation (Chapter 5). Interestingly this hybridisation is not the only way that a noble gas configuration can be attained. Particularly the smallest carbon has a trend to attain octet through multiple covalent bonds, which trend decreases sharply to silicon and to the other members of the group. Carbon forms multiple bonds of the type $\rangle C = C\langle$, $\rangle C = O$, $\rangle C = S$ $-C \equiv N$, etc.

Table 17.1. Electronic Configurations and Some Properties of Group IVB Elements

Element	Atomic Number	Electronic Configuration	Ionisation Potential (*ev*)	Electronegativity
C	6	$[He]2s^22p^2$	11.25, 24.38, 47.87, 64.48	2.50
Si	14	$[Ne]3s^23p^2$	8.15, 16.34, 33.46, 45.13	1.74
Ge	32	$[Ar]3d^{10}4s^24p^2$	7.88, 15.93, 34.23, 45.7	2.02
Sn	50	$[Kr]4d^{10}5s^25p^2$	7.33, 14.63, 30.6, 39.6	1.72
Pb	82	$[Xe]4f^{14}5d^{10}6s^26p^2$	7.41, 15.03, 32.0, 42.3	1.55

The electronegativities (Table 17.1) expectedly fall from carbon to lead although not quite regularly. On the whole the electronegativities are low and hence there is not much tendency to form quadrinegative anions. If it is at all possible to form a quadrinegative anion it should be with carbon. Negative carbon anions are known in Be_2C(*i.e.* C^{4-}), in sodium alkyls, $NaCH_3$(Na^+ and CH_3^-) and alkali metal carbides Na_2C_2(Na^+ and C_2^{2-} ions). The electronegativity difference between carbon (2.50) and fluorine (4.0) is not sufficient enough to induce ionic character in the fluorocarbons. As we descend the group the electronegativity difference with halogens increases and ionic character may appear in compounds such as SnF_4 though not in $PbCl_4$ or $SnCl_4$ (Chapter 5). However SnF_4 is now regarded as polymeric covalent (Part I ; p 342). In essence Fajan's rules hold good.

In general in any group metallic character should increase with increasing atomic number. Unfortunately the charge (+ 4) on the hypothetical cation with the group valence is so very high that even with lead covalence persists. However when the two outer quantum shell *s* electrons are relatively inert, which effect again increases down the group, we obtain distinct metal character in the heavier elements Sn(II) and Pb(II). With germanium still not enough basic character appears. Standard potentials of tin and lead are close, −0.136 and −0.126 volts respectively (Table 17.2), although not in the expected order. The order however shows, in conformity with experiments, that tin is a better reducing agent than lead.

Table 17.2. Some more Properties of Group IVB Elements

Element	Atomic Radius (A)	Ionic Radius (M^{4+})(A)	M.P. (°C)	B.P. (°C)	Density (*g/ml*)	*E*°, volts $M^{2+} + 2e \rightleftharpoons M$
C	0.77	...	3500	4800	3.52*, 2.25+	—
Si	1.17	0.39	1420	1420	2.49	—
Ge	1.22	0.53	959	2700	5.36	—
Sn	1.40	0.71	232	2360	5.77	−0.136
Pb	1.54	0.84	327	1755	11.34	−0.126

* diamond; + graphite

In contrast to carbon, silicon and the other members of the group have dormant *d*-orbitals and hence these later elements can accommodate more than eight electrons around them. Whereas in carbon we have a maximum of co-ordination number four (section 15.2.1) in the others we have six. Carbon—carbon single bond is far stronger than silicon—silicon or germanium—germanium single bonds.

The strength of carbon-carbon single bonds and carbon-carbon multiple bonds helps carbon to form compounds with long chains of identical atoms. *The property of forming compounds with chains of identical atoms is called catenation.* Catenation in carbon compounds may give rise to long straight chain compounds with C-C links (eg: saturated hydrocarbons called alkanes C_nH_{2n+2}) C = C links (eg: *alkenes*, C_nH_{2n}), C ≡ C links (alkynes, C_nH_{2n-2}) as also ring compounds (eg: benzene). The tendency to catenation falls off in the order $C \gg Si > Ge \simeq Sn \gg Pb$. It is interesting to note that although a number of silicon hydrides analogous to saturated paraffin hydrocarbons are known there are as yet no reports of silicon analogues of olefines (alkenes), acetylenes (alkynes) or aromatics. This supports the order of catenation among IVB elements.

According to Fajans' rules the tendency to complexation should be the highest in carbon in +4 state and least in lead. C^{4+} does not exist and indeed the tetravalent carbon compounds have so strong covalent bonds that usual coordinating ligands cannot break such bonds. In the other elements over and above the *s*- and *p*-orbitals, *d*-orbitals are also available and hence they are capable of forming more than four bonds. Thus with later elements adduct formation, such as $SnCl_4$, dipy, is a common feature. On the whole the tendency to complex formation decreases down the group.

In the + 2 state, Fajans' rules predict enhanced tendency to form ions with increasing atomic number. The standard potentials of the M^{4+}/M^{2+} couples are for Sn, + 0.15 volts and for Pb, + 1.8 volts. The values indicate that lead (IV) must be a far stronger oxidant than tin (IV), and conversely tin (II) must be a superior reducing agent than lead (II). This is in complete accord with experimental results. The + 2 state is the common valence state with lead and tin but with the other elements + 4 is the common valence. Remember that the varied valences in this group are due to an *inert pair effect.*

17.1.2. Chemical Behavior. The chemical behaviour may be examined under the + 4 and + 2 states.

A. Quadrivalent State. Hydrides: All the elements form volatile covalent hydrides. The ease of formation decreases down the group. Due to the strong tendency to catenation (being the result of very strong carbon-carbon bonds) carbon forms a vast array of chain and ring compounds including the *alkanes* C_nH_{2n+2}), *alkenes* (olefines) (C_nH_{2n}), *alkynes* (*acetylenes*) (C_nH_{2n-2}) and many aromatic compounds. Silicon forms a few saturated bydrides (Si_nH_{2n+2}) called *silanes.* Acid hydrolysis of magnesium silicide Mg_2Si gives a mixture of SiH_4, Si_2H_6, Si_3H_8, Si_4H_{10} which are then separated and purified by fractional distillation. Germanium forms only a few polynuclear hydrides GeH_4, Ge_2H_6, Ge_3H_8 whereas tin and lead form only SnH_4 and PbH_4. The thermal stability of these hydrides decreases down the group. The reducing properties increase down the group. The ease of syntheses also falls off down the group. Thus SnH_4 and PbH_4 are difficult to prepare and are obtained by the action of $LiAlH_4$ on the tetrahalides:

$$SnCl_4 + LiAlH_4 \rightarrow SnH_4 + LiAlCl_4$$

Electrolysis of $SnCl_2$ or $PbCl_2$ with the respective metal as cathode also produces the hydride.

Oxides and Oxyacids: Carbon dioxide is an acidic oxide reacting with alkali to form normal carbonates and bicarbonates. Silicic acid (freshly precipitated from metal silicates) is highly condensed. It is amphoteric, reacting with bases to form silicates, and with acids like HF to form SiF_4 or H_2SiF_6. The other dioxides GeO_2, SnO_2 and PbO_2 have diminished acidic character, GeO_2 is not as strongly acidic as SiO_2, and SnO_2 and PbO_2 are still amphoteric.

Carbon dioxide is a discrete covalent compound, O = C = O. Two sp_x hybridised orbitals of carbon (with one unpaired electron on each) overlap with p_x orbitals of two oxygens. The p_y orbital of carbon then overlaps with the p_y orbital of one oxygen (both having one unpaired electron). Similar overlap along z axis gives another carbon-oxygen π- bond. Thus CO_2 is made up of two σ- and two π-bonds.

$$\text{C} \quad \frac{\uparrow\downarrow}{2s}\ \frac{\uparrow}{2p_x}\ \frac{\uparrow}{2p_y}\ \frac{\quad}{2p_z} \ \text{hybridises to}\ \frac{\uparrow}{2(sp_x)}\ \frac{\uparrow}{2(sp_x)}\ \frac{\uparrow}{2p_y}\ \frac{\uparrow}{2p_z}$$

$$\text{O} \quad \frac{\uparrow\downarrow}{2s}\ \frac{\uparrow}{2p_x}\ \frac{\uparrow}{2p_y}\ \frac{\uparrow\downarrow}{2p_z}\ \text{and} \qquad \text{O}\ \frac{\uparrow\downarrow}{2s}\ \frac{\uparrow}{2p_x}\ \frac{\uparrow\downarrow}{2p_y}\ \frac{\uparrow}{2p_z}$$

As we come to silicon the available p orbitals, being $3p$, are of larger size and a π-type overlap with oxygen $2p$ orbitals of smaller size becomes less effective.

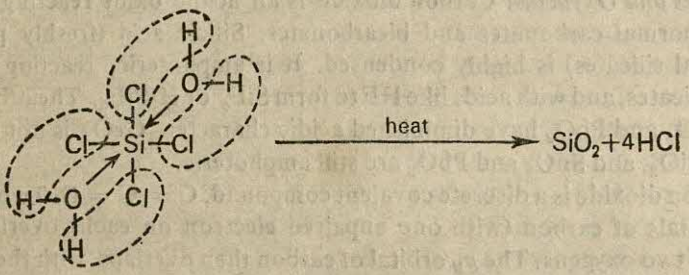
Multiple bonding over a longer internuclear distance is weak compared to multiple bonding over a shorter internuclear distance. Moreover electronegativity difference between silicon and oxygen is much larger than the difference between carbon and oxygen and hence the bonds in silica have considerable ionic character. All these lead to a three dimensional infinite structure in SiO_2 and silicates. Thus CO_2 is a gas and SiO_2 is a high melting solid. However it should be noted that there is no difficulty in getting a good overlap of a silicon 3*d* orbital with a 3*p* orbital of a halogen or an sp^3 hybrid orbital of H_2O molecule.

It may be mentioned here that SiO_2 exists in as many as three crystalline forms with characteristic range of stability. Basically all the forms have SiO_4 tetrahedra linked up with bridging oxygen (as in the silicates) but the details of the tetrahedral arrangement varies:

Quartz	Tridymite	Cristobalite
($< 870°C$)	($870-1470°C$)	($> 1470°C$)

Each of these has an α-form and a β-form—the two forms varying by a slight rotation of the tetrahedra with respect to each other without a change in the overall arrangement of the tetrahedra.

Halides: The tetrahalides are all covalent and tetrahedral (sp^3 hybridisation). Carbon tetrafluoride is very stable and unreactive. Silicon and the other halides are readily hydrolysed. The trend towards hydrolysis decreases down the group. $GeCl_4$ and $GeBr_4$ are less readily hydrolysed than the silicon halides. In order that hydrolysis can occur there must first be a nucleophilic (nucleus seeking a lone pair) attack by H_2O on the parent element of the halide (17-I). Since carbon does not have any *d*-orbital in its outer quantum shell ($n = 2$) for attack by a nucleophile (H_2O) its halides do not suffer any hydrolysis. CCl_4, CF_4 are also coordinatively saturated but this is not the case with $SiCl_4$, $GeCl_4$ which can go upto a coordination number six. Moreover because of electronegativity difference silicon in $SiCl_4$ has more δ^+ charge than carbon in CCl_4. This also facilitates nucleophilic attack by H_2O. The other elements possess vacant *d*-orbitals to which the aqua molecule can get attached and hence they suffer hydrolysis. Because of the availability of *d*-orbitals halo complexes with coordination number six, such as $(NH_4)_2[PbCl_6]$, $H_2[SiF_6]$ etc. are also possible.



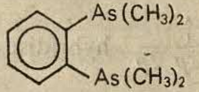
(17–I)

Lead tetrabromide and lead tetraiodide are not known probably because the highly oxidising lead (IV) cannot survive in the presence of the highly reducing bromide and iodide ions. Compare the standard potentials

$$Pb^{4+} + 2e \rightleftharpoons Pb^{2+}\ ; \quad E° = +1.8 \text{ volts}$$

$$I_2 + 2e \rightleftharpoons 2I^-\ ; \quad E° = +0.54 \text{ volts}$$

Complexes: Carbon complexes are little known. Nyholm has prepared complexes with o-phenylenebisdimethylarisine (*diars*) (17-II) by the reaction:

$CCl_4 + 2\ \text{diars} \rightarrow [C(\text{diars})_2]\ Cl_4$;  = diars.

(17–II)

Besides the halo complexes mentioned above, adducts of halides with N, O, P, S donors are also known:

$[SiCl_4.(N(CH_3)_3)_2]$; $[SnCl_4.\text{dipy}]$; $[SiI_2py_4]I_2$; etc.

Availability of *d*-orbitals with silicon, tin, lead doubtless facilitates the formation of the above six-corodinate complexes. Carbon halides are clearly incapable of forming such six-coordinate complexes.

B. Bivalent State: Carbon monoxide is an electron deficient molecule and hence functions as an excellent π-acid (electron acceptor) in metal carbonyls. More on metal carbonyls appears in Chapter 23. Germanium (II) oxide is acidic and is a stronger acid than $Sn(OH)_2$. But $Sn(OH)_2$ is amphoteric reacting with acids to form salts and with alkalies to give stannites M_2SnO_2. But lead hydroxide is more basic than is acidic ($K_A \sim 8 \times 10^{-12}$ and $K_B \sim 1 \times 10^{-13}$). Bivalent tin and lead expectedly give rise to cationic properties. Tin (II) is a strong reducing agent though lead (II) is not.

A lone pair is left on the metal ions in their + 2 state. While it is possible to prepare complexes of these metal ions with donor ligands (eg: $SnCl_2$ reacts with donor solvents L to give $SnCl_2.L$) it is also possible to use $SnCl_2$ or $SnCl_3^-$ as donors to other metal ions. Thus the interaction of platinum group metal salts with $SnCl_2$ leads to the formation of complex anions of Ru(II), Rh(I), Pt(II) which have been isolated as salts of large cations. The anions are formulated as $[RuCl_2(SnCl_3)_2]^{2-}$, $[Rh_2Cl_2(SnCl_3)_4]^{4-}$ and cis/trans $[PtCl_2(SnCl_3)_2]^{2-}$. $SnCl_3^-$ anion is considered to be of the same donor strength as Cl^-. Neutral complexes like $[(Ph_3P)_2\ PtCl(SnCl_3)]$ have also been synthesised. The lone pair left on tin (II) also generates interesting stereochemical features. In $SnCl_2.2H_2O$ one H_2O is loosely bound as it is lost at 80°C. Sn(II) has thus two corodinated Cl^-, one coordinated H_2O and the lone pair occupying the fourth point of the tetrahedron. This structure is often called as Ψ-tetrahedral (Ψ here indicating that a lone pair takes up a coordination site of the metal ion). $SnCl_3^-$ is also Ψ-tetrahedral. Similar Ψ-tetrahedral behaviour for Ge(II) and Pb(II) has not yet been exposed.

17.2. ELEMENTARY FORMS OF THE GROUP IVB ELEMENTS

Carbon exhibits two major allotropic forms (diamond and graphite). These forms are manifestations of attaining a stable noble gas configuration even in the elementary state, and this can be achieved in two ways.

Hybdridisation of carbon $2s$ orbital and the three $2p$ orbitals gives four equivalent sp^3 orbitals each of which contains one unpaired electron. If all the carbons are assumed to have this hybridisation then overlap of these hybrid orbitals of

$$\mathrm{C}\ \underset{2s}{\underline{\uparrow\downarrow}}\ \underset{2p}{\underline{\uparrow}}\ \underset{2p}{\underline{\uparrow}}\ \underset{2p}{\underline{\quad}}\ \text{ hybridises to }\ \underset{2(sp^3)}{\underline{\uparrow}}\ \underset{2(sp^3)}{\underline{\uparrow}}\ \underset{2(sp^3)}{\underline{\uparrow}}\ \underset{2(sp^3)}{\underline{\uparrow}}$$

neighbouring carbon atoms will lead to a non-ending tetrahedral structure (Fig.17.1*a*). This is what obtains in diamond. Diamond thus has covalent bonds but these bonds do not end to produce discrete 'molecules', instead three dimensional 'giant' 'molecules' are formed. Diamond is, therefore, an extremely hard and high melting substance. The C—C bonds (length 1.54A) are extraordinarily stable, the non-volatility (sublimes at 3500°C) reflecting the difficulty of breaking these bonds. Diamond scratches all other metals. Tips of cutting tools are often set with diamond.

An alternative hybridisation of the $2s$ and two $2p$ orbitals gives three equivalent sp^2 hybrid orbitals at 120° to each other on the same plane. The third $2p$ orbital is perpendicular to the plane of the sp^2 orbitals. If all carbons are assumed to

$$\mathrm{C}\ \underset{2s}{\underline{\uparrow\downarrow}}\ \underset{2p}{\underline{\uparrow}}\ \underset{2p}{\underline{\uparrow}}\ \underset{2p}{\underline{\quad}}\ \text{ hybridises to }\ \underset{2(sp^2)}{\underline{\uparrow}}\ \underset{2(sp^2)}{\underline{\uparrow}}\ \underset{2(sp^2)}{\underline{\uparrow}}\ \underset{p}{\underline{\uparrow}}$$

have this hybridisation, and if each carbon overlaps with three neibhbouring carbon atoms we have a non-ending two dimensional hexagonal planar structure (Fig. 17.1b). The third $2p$ orbital of each carbon of C_6 hexagonal unit then overlaps with each other to form a π-type molecular orbital. This is equivalent to a resonating alternate double bond on the valence bond model. More than one such layer is possible, and these layers have a weak van der Waals type force between them. This structure prevails in graphite. The ability of the planar layers to slip over one another makes graphite a good lubricant. Our 'lead' pencils are really made of graphite and their layers of graphite rub off as we write. Graphite too has a high

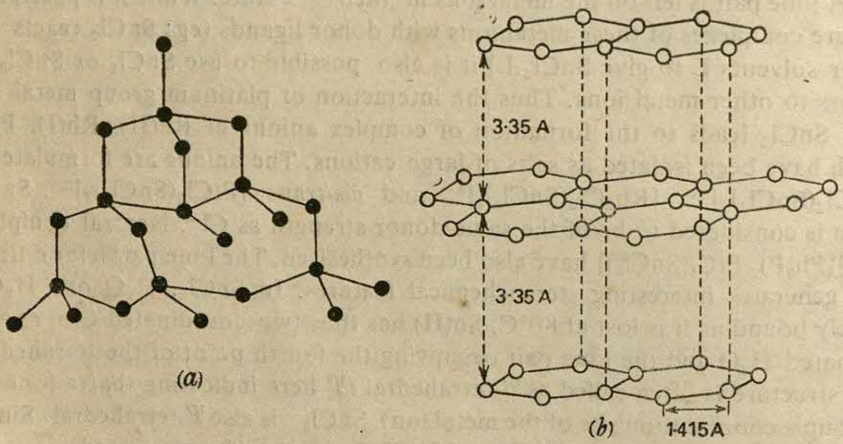


Fig. 17.1. Models of (a) diamond and (b) graphite

melting point (~3500°C) since the bonds within the polymeric layer is quite tough. Because π-electrons are mobile (not being restricted between two atoms) graphite can conduct electricity but diamond cannot. Graphite is found in nature in mines in several countries. Ceylon graphite is purest. Siberian and Bohemian varieties are used in pencils. Artificial graphite is manufactured by heating (~ 2500°C) electrically a mixture of sand and anthracite or coke for about thirty hours. The presence of sand presumably catalyses the conversion to graphite. Graphite finds extensive use in dry batteries and as electrodes. Graphite can be changed to diamond by the application of high pressure and high temperature (~ 3000°C). An inspection of the densities of graphite and carbon (Table 17.2) shows that pressure must be applied to enhance the conversion of graphite to diamond.

Besides diamond and graphite there are several other forms of carbon collectively called as amorphous carbon, such as charcoal, soot, lampblack. These are really inferior, microcrystalline varieties of graphite. The amorphous forms contain only a few unit cells of the graphite structure. The physical properties of these varieties depend on their surface areas. The finely divided forms contain vast surface areas and are capable of absorbing large amounts of solutes from solution as also gases. When vegetable substances such as wood, sugar are heated to ~ 300°C in the absence of air a black residue is obtained. This is called *charcoal.* An animal source under similar treatment gives animal charcoal. The adsorptive capacity of charcoal can be increased by treatment with steam or with air-steam mixtures for long periods at high temperatures. This treatment increases the porosity and also removes hydrocarbons. Thus treated, charcoal is called *active charcoal.* Active charcoal is used in adsorption of gases and colouring matter, and in decolourising sugar syrup. It also has use as a catalyst.

Silicon and germanium occur in one structural form, that of diamond. With increasing atomic number metallic bonding predominates. Since the heavier elements cannot participate in strong multiple bonding the graphite structure does not appear beyond carbon. Table 17.3 gives a summary of the crystal structures of the group IVB elements.

Table 17.3. Crystal Structures of Group IVB Elements

Structure Type	Carbon	Silicon	Germanium	Tin	Lead
Diamond	Yes	Yes	Yes	Yes (<13°C)	No
Graphite	Yes	No	No	No	No
Metallic	No	No	No	Yes (>13°C)	Yes

Intercalation Compounds of Graphite: The sp^2 hybridisation of carbon in graphite may be partially changed to sp^3, maintaining the layer structure. Such compounds are known as intercalation compounds of graphite. Thus fluorine reacts with graphite to give a white polymeric compound $(CF)n$. Interlayer spacings in $(CF)_n$ vary in the range 6.9–8.2A. The C—C bond distance is 1.54A. The specific resistance of $(CF)_n$ is 10^6 times larger than that of graphite. The carbons have tetrahedral chair conformation. The reacting species, here fluorine, penetrate the graphite structure between the layers. Bromine and chlorine (X) also form intercalation compounds of a different formula C_8X. These compounds are more conducting than graphite indicating that graphite layer has donated electrons to bromine and chlorine. We may represent these compounds as $C_8^+X^-$. Intercalation results in an increase in volume.

17.3. INORGANIC GRAPHITE AND INORGANIC DIAMOND

Boron reacts with nitrogen or ammonia on heating to form a binary nitride BN which is a white, refractory solid. The compound is also obtained by heating ammonium chloride and borax:

$$Na_2B_4O_7 + 2NH_4Cl \xrightarrow{\text{heat}} 2NaCl + 2BN + B_2O_3 + 4H_2O$$

This form of boron nitride is similar to graphite in physical properties and has a graphite-like layer structure of alternate boron and nitrogen. The boron and nitrogen atoms are 1.45A from each other. The layers are at a distance of 3.34A. This form of boron nitride is often called *white graphite*. In this form each boron and nitrogen has sp^2 hybridisation. The overlap of the hybrid orbitals of one boron with three hybrid orbitals of three neighbouring nitrogens

$$\text{Boron} \quad \frac{\uparrow\downarrow}{2s}\ \frac{\uparrow}{2p}\ \frac{\quad}{2p}\ \frac{\quad}{2p} \text{ hybridises to } \frac{\uparrow}{2(sp^2)}\ \frac{\uparrow}{2(sp^2)}\ \frac{\uparrow}{2(sp^2)}\ \frac{\quad}{2p}$$

$$\text{Nitrogen} \quad \frac{\uparrow\downarrow}{2s}\ \frac{\uparrow}{2p}\ \frac{\uparrow}{2p}\ \frac{\uparrow}{2p} \text{ hybridises to } \frac{\uparrow}{2(sp^2)}\ \frac{\uparrow}{2(sp^2)}\ \frac{\uparrow}{2(sp^2)}\ \frac{\uparrow\downarrow}{2p}$$

give three planar bonds at 120° to each other. The lone pair of nitrogen in the remaining $2p$ orbital then forms a π-bond with the vacant $2p$ orbital of boron. Note that $(BN)_3$ is isoelectronic with the C_6 hexagonal structure in graphite. Through resonance all the B-N distance as also the bond order become equivalent. We can also say that the three lone pairs of the three nitrogen atoms of the hexagonal $(BN)_3$ overlap with the three empty p_z orbitals of the three borons giving π-type M.O.'s. The graphite-like variety is used as an antisticking material in moulds in glass industry.

Like the conversion of graphite to diamond, the above layer structure of boron nitride can be converted to the tetrahedral non-ending diamond-like structure. High temperature (18,000°C) and high pressure (85,000 atm.) are required to bring about this conversion. The diamond-like variety of BN is called *borazon*. In borazon each tetrahedral nitrogen is bonded covalently to four tetrahedral boron (and vice versa)—to three borons with usual shared pair covalent bond and to the fourth boron via a coordinate link from nitrogen to boron. Each boron is connected to three nitrogen through shared pair covalent bonds, and to the fourth nitrogen by a coordinate link from nitrogen to boron.

Boron $\underset{2s}{\underline{\uparrow\downarrow}}\ \underset{2p}{\underline{\uparrow}}\ \underset{2p}{\underline{\quad}}\ \underset{2p}{\underline{\quad}}$ hybridises to $\underset{2(sp^3)}{\underline{\uparrow}}\ \underset{2(sp^3)}{\underline{\uparrow}}\ \underset{2(sp^3)}{\underline{\uparrow}}\ \underset{2(sp^3)}{\underline{\quad}}$

Nitrogen $\underset{2s}{\underline{\uparrow\downarrow}}\ \underset{2p}{\underline{\uparrow}}\ \underset{2p}{\underline{\uparrow}}\ \underset{2p}{\underline{\uparrow}}$ hybridises to $\underset{2(sp^3)}{\underline{\uparrow}}\ \underset{2(sp^3)}{\underline{\uparrow}}\ \underset{2(sp^3)}{\underline{\uparrow}}\ \underset{2(sp^3)}{\underline{\uparrow\downarrow}}$

17.4. BINARY CARBIDES

Binary carbides have some superficial resemblances with the binary hydrides with regard to classification: I. Salt-like carbides; II. Covalent carbides and III. Metallic or interstitial carbides.

17.4.1. Salt-like Carbides. These carbides are ionic and expectedly formed by strong electropositive elements of group IA, IIA and IIIA.

These carbides can be classified as (*a*) methanides and (*b*) acetylides. Methanides contain C^{4-} anion and the acetylides C_2^{2-} (i.e. $^-C \equiv C^-$) anion. Salt-like carbides possess ionic crystal lattice. They are easily decomposed by water or dilute acids liberating CH_4 or C_2H_2. Carbides of beryllium (Be_2C) and aluminium (Al_4C_3) are colourless and crystalline with ionic crystal structures. These compounds contain the tetranegative C^{4-} ions and are easily hydrolysed in water giving CH_4.

$$Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4;\ Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$$

Due to this hydrolysis behaviour these carbides are also called methanides. Their synthesis involves combination of the elements at ~ 1500°C.

The commonly called acetylides have two carbon atoms inside the anion which is dinegative. The acetylides are a large group of carbides formed mainly by elements of group I, II and III and to some extent by the lanthanides and by thorium and uranium. Some examples are:

Group I : Na_2C_2, K_2C_2 etc; Cu_2C_2, Ag_2C_2
Group II : BeC_2, MgC_2, CaC_2, ZnC_2
Group III : Al_2C_6, LaC_2
Group IV : ThC_2
Group VI : UC_2

Calcium acetylide, commonly known as calcium carbide, is obtained by heating a mixture of CaO and coke to ~ 300°C in an electric furnace: $CaO + 3C \rightarrow CaC_2 + CO$. Calcium acetylide collects at the bottom and is tapped off from time to time (Chapter 15). It finds use in the preparation of acetylene and calcium cyanamide — a nitrogenous fertiliser:

$$CaC_2 + 2HCl \rightarrow CaCl_2 + C_2H_2;\ CaC_2 + N_2 \rightarrow CaN.CN + C$$

The acetylides of Cu, Ag, Zn, Mg are prepared by passing acetylene through solutions of the metal salts. Ammoniacal solutions of copper (I) and silver (I) are used for the synthesis of Cu_2C_2 and Ag_2C_2 while petrol solutions of dialkyl zinc and dialkyl magnesium are used for ZnC_2 and MgC_2. The compounds react with water and produce acetylene:

$$MgC_2 + 2H_2O \rightarrow Mg(OH)_2 + H_2C_2$$

All acetylides have ionic sodium chloride structure.

17.4.2. Covalent Carbides. Depending on volatility these covalent carbides can be subdivided into two classes. The first class consists of small discrete molecules, formed especially by hydrogen and the elements of groups VIB and VIIB. Examples are CH_4, CO_2, CS_2, CCl_4 etc. The second class forms giant molecules although the bonding is still covalent. The most known compound is *carborundum* (SiC) which is a very hard solid decomposing above 2200°C and has a diamond like lattice. This is made by reducing SiO_2 with carbon in an electric furnace. This is widely employed as an abrasive and a refractory material. Its crystal structure reveals that each of the carbon (or silicon) is tetrahedrally surrounded by atoms of the other element.

17.4.3. Interstitial Carbides. Close packed structures of metals have holes in the lattice. These holes are of two kinds: octahedral holes created by close packing of six metal atoms in octahedral positions and tetrahedral holes created by some metals positioned in tetrahedral points. The small carbon atoms can sometimes be fitted into holes of suitable sizes (which are dependent on the size of the metal atoms) and naturally the radius ratio rules (Chapter 6) will dictate the formula of such interstitial carbides. From our discussion in Chapter 6 it can be inferred that carbon/metal ratios should be ~ 0.4 to 0.7 for octahedral holes (NaCl structures). Investigations on the structures of several interstitial carbides show that critical radius ratio is ~ 0.6. Taking the covalent radius of carbon as 0.77A it can be inferred that the atomic radius of the metal must be from 1.3A to 1.9A so as to have such an octahedral hole fitting. Metals like Cr, Mn, Fe, Co, Ni have their atomic radii less than 1.3A and hence do not form carbides of this type. On the other hand Ti, Hf, W, Nb, have their radii larger than 1.3A and hence form interstitial carbides: TiC, HfC, W_2C, NbC etc. Such compounds have conductivity, metallic lustre like metallic alloys and the forces between the metal atoms are very much like those in the metal itself. The insertion of carbon atoms results in an increase in volume (~ 9%).

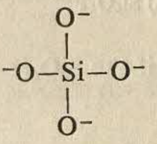
Many of these carbides have very high melting points:

Carbide	TiC	ZrC	TaC	NbC	MoC
M. P. (°C)	3150	3500	3800	3500	2965

These are very hard, their hardness being in between those of diamond and topaz. Interstitial carbides are formed by heating the metal or its oxide with carbon. Because of the formation of very stable interstitial carbides, carbon reduction of metal oxides is not preferred for extraction of titanium, zirconium, tungsten etc.

17.5. SILICATES

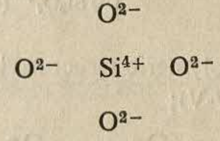
17.5.1. General Considerations. Silicates are the most abundant components of the earth's crust. Silicon and oxygen together make up almost 75% by weight of the earth's crust. The unique feature of all silicate minerals is the tetrahedral coordination of silicon by oxygen. The difference in electronegativities of silicon and oxygen is 1.7 and this large difference suggests considerable ionic character of the bond. Silicon-oxygen bond must be considered, therefore, to have both ionic and covalent characters. The following two extreme structures (17-III and 17-IV) must be considered to contribute to the real structure:



$$\begin{array}{c} O^- \\ | \\ {}^-O-Si-O^- \\ | \\ O^- \end{array}$$

(17-III)

and



$$\begin{array}{ccc} & O^{2-} & \\ O^{2-} & Si^{4+} & O^{2-} \\ & O^{2-} & \end{array}$$

(17-IV)

A silicate, say Mg_2SiO_4, can then be viewed as a salt made up of Mg^{2+} and covalent SiO_4^{4-} or as a complex oxide made up of Mg^{2+}, Si^{4+} and O^{2-} ions. It then follows that isomorphous replacement of cations by other cations of comparable size and charge will be a common feature of silicate composition and structure. The metal ions are so arranged in the silicate crystal lattice that they have their preferred coordination numbers and stereochemistry, being surrounded by requisite number of silicate oxygens in suitable positions. Within some wide limits metal ions of comparable size and coordination number, which are interchangeable are: Mg^{2+} (coordination number 6, ionic radius 0.65A); Fe^{2+}(6, 0.8A); Na^+(6, 0.95A); Ca^{2+} (6, 0.99A) etc. Furthermore the Al^{3+}: O^{2-} radius (0.52A; 1.4A) ratio (0.36) is close to the critical value for transition from coordination number 6 to 4 (Chapter 6) and hence Al^{3+} can even replace Si^{4+} (0.39A) in addition to replacing other cations in octahedral sites. For every aluminium so introduced into the silicate tetrahedra a corresponding substitution of Ca^{2+} for Na^+, Al^{3+} for Mg^{2+} etc must occur in order to maintain electroneutrality.

Tetrahedral SiO_4 units may be linked together by sharing corners but not edges or faces. Thus discrete SiO_4^{2-} units as also infinite chains, rings, sheet and three dimensional framework structures are possible.

17.5.2. Classification and Structure of Sliicates. Some possible closed silicon-oxygen groupings in silicates are shown in Fig. 17.2. These include (*a*) isolated tetrahedra SiO_4^{4-} (*orthosilicates*, Mg_2SiO_4), (*b*) tetrahedra sharing one oxygen atom $Si_2O_7^{6-}$ (*thortveitite*, $Sc_2Si_2O_7$), (*c*) tetrahedra sharing two oxygen atoms to form a three membered ring structure $Si_3O_9^{6-}$ (*benitoite*, $BaTiSi_3O_9$) and (*d*) tetrahedra sharing two oxygen atoms forming a six-membered ring $Si_6O_{18}^{12-}$ (beryl, $Be_3Al_2Si_6O_{18}$). Note that the silicon-oxygen links of Fig. 17.2 are not wholly covalent. They possess substantial ionic character. It is necessary to point out that these structures are not the only possible ones for silicates. For example,

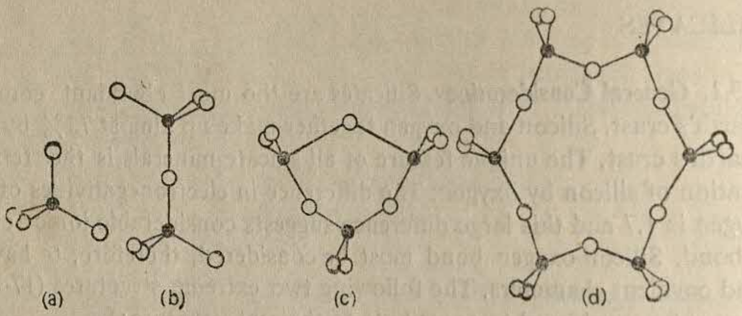
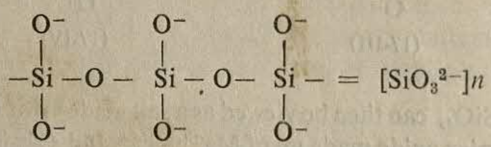


Fig. 17.2. Some possible closed silicon-oxygen groupings in silicates: (a) SiO_4^{4-} (b) $Si_2O_7^{6-}$ (c) $Si_2O_9^{6-}$ (d) $Si_6O_{18}^{12-}$

an open chain polymeric structure is possible if the SiO_4^{4-} tetrahedra share two oxygen atoms (17-V);

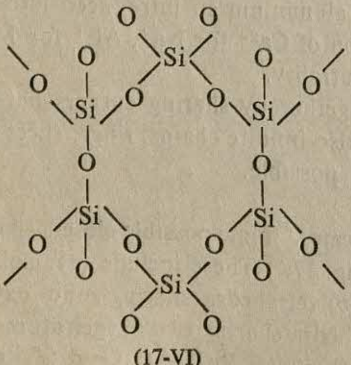


$$\begin{array}{ccccccc} & O^- & & O^- & & O^- & \\ & | & & | & & | & \\ - & Si & -O- & Si & -O- & Si & - = [SiO_3^{2-}]n \\ & | & & | & & | & \\ & O^- & & O^- & & O^- & \end{array}$$

(17-V)

This structure is found in *pyroxenes* ($MgSiO_3$, $Ca(Mg)(SiO_3)_2$, $LiAl(SiO_3)_2$). The second compound is an example of isomorphous replacement of two divalent cations. and the third illustrates replacement of two divalent ions in the second compound by mono- and trivalent cations. A linear net structure is attained in $(Si_4O_{11})^6{}_n{}^-$ when SiO_4^{4-} tetrahedra share alternately two and three oxygen atoms (17-VI):

Amphiboles ($Ca_2Mg_5(Si_4O_{11})_2(OH)_2$) belong to this class, the hydroxy groups being associated with the cations in the crystal. Isomorphous replacement of the cationic metal ions such as Fe for Mg, Na and Al for two Mg, and also of Al for Si in the SiO_4^{4-} tetrahedra is very common in this series.



(17-VI)

When the SiO_4^{4-} tetrahedra are so linked that three of the four oxygen atoms are shared with neighbouring tetrahedra on the same plane a two dimensional net work results giving the anion $(Si_4O_{10})^{4-}$. Examples are *talc*, $Mg_3(OH)_2[Si_4O_{10}]$ and *mica* $KAl_2,(OH)_2[Si_3AlO_{10}]$, $KMg_3(OH)_2[Si_3AlO_{10}]$ etc.

When all four oxygen atoms of the SiO_4^{4-} tetrahedra are shared with neighbouring tetrahedra we get an infinite three dimensional framework with oxygen-silicon ratio of 2:1. Examples of this class are rather extensive. *Felspars* belong to this class: *anorthite*, $Ca[Al_2Si_2O_8]$, *albite*

$Na[AlSi_3O_8]$, *orthoclase*, $K[AlSi_3O_8]$ etc. Note the replacement of silicon of some tetrahedra by aluminium. A second family of such silicates is the *zeolites* which are hydrated silicates. Although the zeolites are similar in many respects to the felspars, the linking of AlO_4 and SiO_4 tetrahedra is such as to leave big holes in the lattice. These holes are not only large enough to accommodate ions such as Na^+ and K^+ but can also accommodate small molecules like CO_2, N_2, CH_3OH, H_2O etc. The structure is very complex but their importance lies in their ability to exchange ions or gas molecules readily. A series of complex sodium alumino silicates (sodium zeolite e.g.: *chabazite*, $Na_2[Al_2Si_4O_{12}]$) possess the property of exchanging their sodium ion for calcium or magnesium ion in solution. The calcium (or magnesium) zeolite can again be regenerated by treatment with concentrated sodium chloride, which reverses the equilibrium to the sodium zeolite:

$$Na_2\,\text{zeolite} + Ca^{2+}\,(\text{or } Mg^{+2}) \rightleftharpoons Ca(\text{or } Mg)\,\text{zeolite} + 2Na^+$$

Zeolites thus perform the purpose of water softeners. These zeolites also serve, by virtue of their capacity to accommodate small molecules, as *molecular sieves*. Zeolites will hold only those small molecules which can readily enter the open cavities of the zeolite structure. The molecules are held in the cavities by weak van der Waals force so that these can be removed by heating and the zeolite thus regenerated to serve as molecular sieve. Zeolites do not absorb any molecule which is too big for their cavities. Organic solvents are now kept dry by leaving them over suitable molecular sieves which can trap H_2O molecule.

Synthetic silicate materials have been made which possess the same exchange properties as the natural zeolites. These *synthetic zeolites* are sodium aluminosilicates of the general formula $Na_2O.Al_2O_3$, $n SiO_2.m H_2O$. On increasing the proportion of SiO_2 the base exchange capacity is lost and the material becomes glassy with $n > 3$. Slow and careful crystallisation (under precisely regulated conditions) of a sodium aluminosilicate gel of proper composition (using reactive forms of silica and alumina gels with sodium salt) gives a synthetic zeolite $Na_{12}\,Si_{12}\,[Al_{12}O_{48}]\,27H_2O$. On dehydration at 350°C under vacuum the water molecules occupying the cavities are removed and the zeolite is ready to serve as molecular sieve.

Another interesting group of synthetic sodium aluminium silicates is *ultramarine blue*. In addition to the silicon-aluminium-oxygen framework the ultramarine contains sulphate and sulphide ions. Commercial ultramarine blue is formed on heating in air a mixture of sodium carbonate (or sodium sulphate), kaolin, wood charcoal (as a carbonaceous reducing agent) and sulphur. Blue ultramarine is $Na_8Al_6Si_6O_{24}S_2$. Like the zeolites the alkali ions of ultramarine can be exchanged with other cations. The $[Al_6Si_6O_{24}]^{6-}$ unit has holes characteristics of the zeolite. The reason for the rich colour is as yet an unsolved problem. A reasonable guess is charge transfer transition. While sulphide ion can serve as a possible reductant in such transition it is difficult to ascertain which metal ion serves as the oxidant. Ultramarine blue is a commercial pigment.

17.6. COMPOUNDS OF THE GROUP IVB ELEMENTS

17.6.1. Halides. All the four tetrahalides of carbon, silicon, germanium and tin are known. With lead only the tetrachloride is known. SnF_4 appears to have a polymeric six-coordinate structure with four bridging equatorial fluorines and two non-bridging axial fluorines (cf: Part I, p. 342). All others are covalent as revealed by their volatility and non-conducting behaviour. There are a few interesting points of comparison: (1) The carbon halides are highly resistant to hydrolysis, this being due to the non-availability of a *d*-orbital for nucleophilic attack by H_2O (17.1.2), (2) CBr_4 and CI_4 decompose below their boiling points whereas $SiBr_4$, SiI_4, $GeBr_4$ do not. This is presumably due to larger halogens clustering around a small carbon atom, (3) Contrary to usual behaviour of covalent compounds $SiCl_4$ has a lower B. P. than CCl_4.

	CCl_4	$SiCl_4$	$GeCl_4$	$SnCl_4$	$PbCl_4$
B. P. (°C)	76.4	57	86.5	114.1	~150

This anomaly has been explained on the assumption of multiple bonding between silicon *d*-orbital and filled *p*-orbital of chlorine (Fig. 17.3) so that there is an effective decrease in the intermolecular van der Waals' forces in silicon halides compared to that in carbon halides. For the other halides boiling points are normal. Syntheses of the important halides appear in subsequent sections.

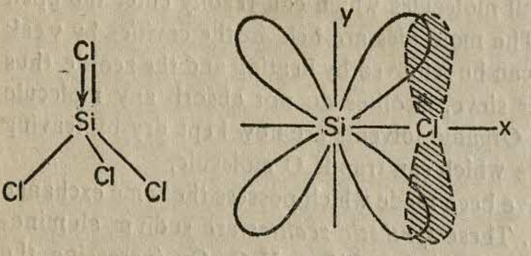


Fig. 17.3. Bonding in $SiCl_4$ showing overlap of a vacant silicon *d* orbital (d_{xy}) with a filled chlorine *p*-orbital (py).

17.6.2. Freons. Mixed chloride fluorides of carbon are today valuable refrigerants. Engineers were searching a refrigerant chemical ,which will be non-toxic, odourless, volatile, non-inflammable, non-corrosive and of course less expensive. Midgley, an American engineer, noted that elements on the right hand side of the Periodic Table were the only ones that formed sufficiently volatile compounds. Inflammability of the compounds also showed a decreasing trend from left to right of the Table, and toxicity increased in a group from top to bottom. A combination of all these ideas led to the discovery of a series of mixed chloride fluorides of carbon, which had the right properties as refrigerant chemicals. These fluoride chlorides are called *freons*. These are conveniently made by passing CCl_4 over CoF_3 at 150–200°C when a mixture of CCl_3F, CCl_2F_2, $CClF_3$ and CF_4 is obtained. These can be separated by making use of the difference in their volatility. CCl_2F_2 has also been obtained by the action of HF on CCl_4 in the presence of $SbCl_3$. $CHClF_2$ is also considered as a freon and is obtained by the reaction of $CHCl_3$ and HF in the presence of $SbCl_5$ as a catalyst:

$$CHCl_3 + 2HF \xrightarrow{SbCl_5} CHClF_2 + 2HCl$$

Recall that carbon has no *d*-orbitals and that in quadrivalent state it has attained noble gas configuration. There is no scope for further reaction. Since fluorine is the most electronegative element the polarity of C—F bonds is such that we may conceive carbon to have undergone some slight oxidation ($C^{\delta+}—F^{\delta-}$). All these explain the inertness of freons to chemical reagents like H_2O, O_2 etc.

17.6.3. Teflon: This is polytetrafluoro ethylene, $(C_2F_4)_n$. This is obtained by the pyrolysis of the freon $CHClF_2$ at 250°C to give first the

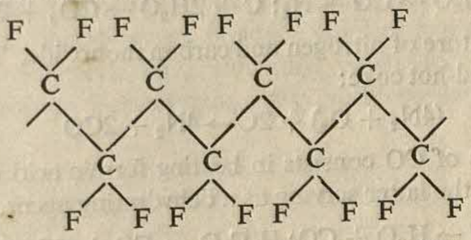
$$2CHClF_2 \xrightarrow{250°C} \underset{(b.p.-76°C)}{CF_2 = CF_2} + 2HCl$$

monomer C_2F_4 which is then polymerised in contact with an aqueous solution of a peroxy-disulphate or oil-soluble peroxides under moderate pressure and low temperature.

$$n\,(CF_2 = CF_2) \longrightarrow [CF_2—CF_2]_n$$

This is a white solid with good electrical insulating properties and exceptional resistance to chemical attack. It is insoluble in any solvent.

The polymer comprises a straight backbone of carbon atoms symmetrically surrounded by fluorine atoms:



It is now extensively used in electrical insulation, high-temperature industrial plastics, cooking utensils, chemical equipments etc.

17.6.4. Carbon Tetrachloride. This is made by passing a mixture of CS_2 and Cl_2 through a red hot tube:

$$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$$

Sulphur monochloride boils at 138°C whereas CCl_4 boils at 78°C so that CCl_4 can be separated from S_2Cl_2 by fractional distillation. It is used widely as an organic solvent for non-polar substances, in dry cleaning and in putting out oil fires.

17.6.5. Carbon Disulphide. This is prepared technically by the direct combination of red hot charcoal and sulphur vapour in an electric furnace:

$$C + 2S \rightarrow CS_2$$

The charcoal is admitted at the top of the furnace and sulphur at the side of the furnace. An arc is set between two carbon electrodes near the base of the furnace.

Carbon disulphide vapour passes up the stack of charcoal and escapes through outlet at the top. The gas is passed through a water cooled condenser and collected. It is highly inflammable. It is used as a solvent in the manufacture of CCl_4, viscose rayon and in vulcanising of rubber. By virtue of its poisonous nature this is also used in keeping off rats from grain storage houses. Some reactions of this compound are given below :

$$CS_2 + 3Cl_2 \longrightarrow CCl_4 + S_2Cl_2$$

$$CS_2 + 2H_2O \xrightarrow{150°C} 2H_2S + CO_2$$

$$CS_2 + 4K \longrightarrow 2K_2S + C$$

$$3CS_2 + 6NaOH \longrightarrow Na_2CO_3 + 2Na_2CS_3 \text{ (thiocarbonate)} + 3H_2O$$

17.6.6. Carbon Monoxide. At ~1000°C excess carbon and oxygen produce CO:

$$2C + O_2 \rightarrow 2CO$$

Artificial fuel gases which contain CO as an important constituent include water gas and producer gas. The former is obtained by the interaction of red hot coke and steam:

$$C + H_2O \rightarrow CO + H_2;\ C + 2H_2O \rightarrow CO_2 + 2H_2$$

Producer gas is a mixture of nitrogen and carbon monoxide. This is made by the passage of air over red-hot coke:

$$(4N_2 + O_2) + 2C \rightarrow 4N_2 + 2CO$$

Laboratory synthesis of CO consists in heating formic acid or oxalic acid with concentrated H_2SO_4, the latter serving as a dehydrating agent. The CO_2 liberated

$$HCOOH \rightarrow H_2O + CO;\ H_2C_2O_4 \rightarrow CO + CO_2 + H_2O$$

in the second case is absorbed in alkali. Carbon monoxide is extraordinarily poisonous. It combines with hemoglobin of blood and thus renders the red blood cells incapable of functioning as oxygen carriers. (Chapter 10.19)

Carbon monoxide is an electron deficient molecule and has π-acceptor properties. It is an ideal ligand for low oxidation states of metals. Details of the structure of CO and metal carbonyls appear in Chapter 23.

17.6.7. Cyanogen and Hydrocyanic Acid: We have already seen (section 14.4.10) that KCN is obtained when NH_3 gas is led over a fused mixture of K_2CO_3 and carbon. Double decomposition between solutions of KCN and $AgNO_3$/ $HgCl_2$ provides precipitate of AgCN and $Hg(CN)_2$ respectively. When these cyanides are heated corresponding metals and cyanogen gas (C_2N_2) are obtained.

$$K_2CO_3 + C + 2NH_3 \rightarrow 2KCN + 3H_2O$$

$$AgNO_3 + KCN \rightarrow AgCN + KNO_3$$

$$2AgCN \rightarrow 2Ag + C_2N_2;\ Hg(CN)_2 \rightarrow Hg + C_2N_2$$

This gas is also obtained when cupric salts react with KCN:

$$CuSO_4 + 2KCN \rightarrow K_2SO_4 + Cu(CN)_2$$
$$2Cu(CN)_2 \rightarrow Cu_2(CN)_2 + (CN)_2$$

The gas is hydrolysed by water:

$$(CN)_2 + H_2O \rightarrow HCN + HCNO$$

Its structure may be represented as: $N \equiv C-C \equiv N$:, the two carbons being *sp* hybridised (c.f.: section 20.4). The C-C bond distance is 1.36A.

HCN gas is liberated whenever a metal cyanide is treated with an acid:

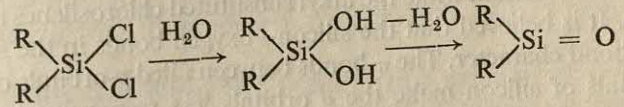
$$KCN + HCl \rightarrow KCl + HCN$$

It is also obtained when dry $Hg(CN)_2$ is reacted with dry H_2S:

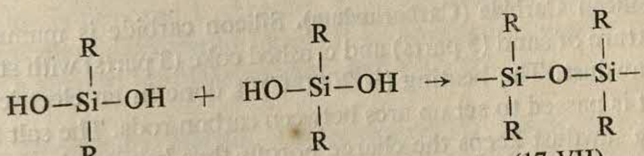
$$Hg(CN)_2 + H_2S \rightarrow HgS + 2HCN$$

It is a dangerous gas. Intake of a small amount may prove fatal. It may be of interest to note that the cyanide ion is the strongest known ligand and is placed at the very end of the spectrochemical series (Chapter 10).

17.6.8. Silicones : These are some polymeric organosilicon compounds with carbon-silicon and silicon-oxygen bonds. Complete hydrolysis of silicon tetrachloride leads to polymeric SiO_2. But alkyl substituted chlorosilanes respond differently to hydrolysis. For example, dialkyl dichlorosilanes do not give dialkyl silicon oxide



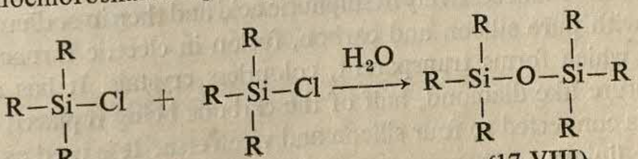
but polymeric compounds called silicones (17-VII):



$$HO-\underset{R}{\overset{R}{Si}}-OH + HO-\underset{R}{\overset{R}{Si}}-OH \rightarrow -\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-$$

(17-VII)

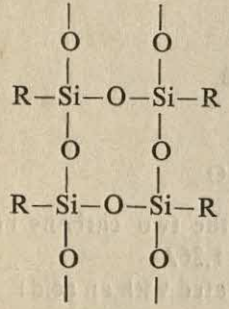
Trialkyl monochlorosilanes R_3SiCl produce hexaalkyl disiloxanes (17-VIII):



$$R-\underset{R}{\overset{R}{Si}}-Cl + R-\underset{R}{\overset{R}{Si}}-Cl \xrightarrow{H_2O} R-\underset{R}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}-R$$

(17-VIII)

Hydrolysis of alkyl trichlorosilanes, $RSiCl_3$, gives a complex cross linked polymer (17-IX). The degree of cross linking and the nature of the products depends not only on the substituents but also on the condition of hydrolysis. The intermediate, alkyl/aryl chlorosilanes, necessary for the manufacture of the above silicones have been obtained by a variety of methods:



(17-IX)

(1) Reaction of $SiCl_4$ with suitable Grignard reagents:

$$SiCl_4 + CH_3MgI \rightarrow SiCH_3Cl_3(\text{also } Si(CH_3)_2Cl_2 \text{ and } Si(CH_3)_3Cl) + MgClI$$

(2) Reaction of silicon and alkyl halides with zinc or aluminium which function as halogen acceptors:

$$SiCl_4 + 3CH_3Cl + 2Al \rightarrow CH_3SiCl_3 + (CH_3)_2AlCl + AlCl_3$$

(3) Reaction of methyl chloride with copper-activated silicon at 300°C:

$$CH_3Cl + Si(Cu) \rightarrow (CH_3)_n\, SiCl_{4-n}\ (n = 1 \text{ and } 2)$$

It should be appreciated that availability of *d*-orbitals in silicon makes the hydrolysis reactions of alkyl substituted chlorosilanes possible, and also that the silicone frameworks involve tetrahedral silicon.

Silicone polymers may be liquids, rubbers or solids and may possess high stability, resistance to oxidation and chemical reagents, lubricating properties and water repellent properties. These are used in cosmetics, in lubrication, as antifoams, as water repellent, as stop-cock grease etc. One may wonder why the silicones are water resistant while the alkyl substituted chlorosilanes readily undergo hydrolysis. It is believed that the silicon—oxygen bonds in the silicones have some double bond character. The π-bonds between filled *p*-orbitals of oxygen and empty *d* orbitals of silicon make the *d* orbitals less responsive to nucleophilic attack by H_2O.

17.6.9. Silicon Carbide (Carborundum). Silicon carbide is manufactured by heating a mixture of sand (5 parts) and crushed coke (3 parts) with small amount of salt and sawdust. The heating (~ 2000°C) is done in an electric furnace. A heavy current is passed to set up arcs between carbon rods. The salt functions as a flux and the sawdust keeps the charge porous thus helping the escape of CO. The carbon monoxide keeps burning at the top of the charge. The crude product

$$SiO_2 + 3C \rightarrow SiC + 2CO$$

is crushed and washed successively in sulphuric acid and then in sodium hydroxide.

Starting with pure silicon and carbon, fusion in electric furnace gives pure carborundum which forms transparent, colourless crystals. It has a polymeric covalent structure like diamond, half of the carbons being replaced by silicons. Each carbon is connected to four silicon and vice versa. It is used as an abrasive and in furnace linings.

17.6.10. Fluorosilicic Acid. Sillicon tetrafluoride is conveniently made by treating a mixture of fluoride and silica with concentrated sulphuric acid:

$$2CaF_2 + 2H_2SO_4 + SiO_2 \rightarrow 2CaSO_4 + SiF_4 + 2H_2O$$

Silicon tetrafluoride is hydrolysed by water to SiO_2 and H_2SiF_6:

$$3SiF_4 + 2H_2O \rightarrow SiO_2 + 2H_2SiF_6$$

Fluorosilicic acid is better prepared by percolating aqueous HF through a bed of sand:

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$$

The anhydrous acid is unknown. On concentrating an aqueous solution the acid decomposes to SiF_4 and HF. The acid solution is completely hydrolysed by alkali:

$$H_2SiF_6 + 2NaOH \rightarrow Na_2SiF_6 + 2H_2O$$

$$Na_2SiF_6 + 4NaOH \rightarrow 6NaF + SiO_2 + 2H_2O$$

17.6.11. Silicon Chloroform. Silicon analogue of chloroform is prepared by passing HCl gas over silicon at a dull red heat:

$$Si + 3HCl \rightarrow SiHCl_3 + H_2;\ Si + 4HCl \rightarrow SiCl_4 + 2H_2$$

The liquid is condensed in a freezing mixture, and the condensed liquid fractionated to separate $SiHCl_3$ (B. P. ~ 32°C) from $SiCl_4$ (B.P. ~ 57°C). Silicon chloroform is a colourless, fuming and inflammable liquid: It burns in air with a green edged flame emitting white fumes of silica:

$$4SiHCl_3 + 2O_2 \rightarrow SiO_2 + 2H_2O + 3SiCl_4$$

Silicon bromoform and iodoform may be obtained by the action of HBr or HI on silicon, and purifying the product by fractionation.

17.6.12. Silica Gel. When HCl is added to a solution of sodium silicate a transparent colloidal dispersion of hydrated silicon dioxide is first formed. The dispersion soon sets to a firm translucent jelly. When most of the water of hydrated silicon dioxide is removed by heating, a product named *silica gel* is obtained. This is an excellent dehydrating agent. It is also used as catalyst for petroleum cracking, as a support for other catalysts like V_2O_5 etc.

17.6.13. Germanium Halides. Concentrated HF reacts with GeO_2 to give colourless hygroscopic crystals of $GeF_4.3H_2O$. Potassium fluoride reacts with an aqueous solution of the tetrafluoride to give the potassium salt of fluorogermanate $K_2[GeF_6]$. Germanium tetrachloride is made by heating germanium in a stream of chlorine or by reacting GeO_2 with fuming hydrochloric acid. From HCl solution of $GeCl_4$, salts of $H_2[GeCl_6]$ can be obtained by the addition of heavy alkali ions.

17.6.14. Stannous Chloride. Metallic tin (Sn^{2+}/Sn; $E° = -0.136$ volt) liberates hydrogen from hydrochloric acid to form $SnCl_2$ which crystallises as the dihydrate. The anhydrous salt can be prepared by heating the metal in an atmosphere of dry

HCl gas. Solution of $SnCl_2$ is protected against oxidation and hydrolysis by maintaining the solution acidic (HCl) and adding tin pieces. It is used as a reducing agent—reducing Fe^{3+} to Fe^{2+}, Hg^{2+} to $Hg^{2}{}_{2}{}^{+}$, Cu^{2+} to Cu^{+} and organic nitro-compounds to amino compounds. It is used in mordant dying (Chapter 16).

17.6.15. Stannic Chloride. This is made by oxidising tin by gaseous chlorine and condensing the gas. It is collected as a colourless liquid being protected from moist air by a $CaCl_2$ guard tube. Because of the availability of *d*-orbitals stannic halides are readily hydrolysed, and also readily form halo complexes.

$$SnCl_4 + 4H_2O \rightarrow 4HCl + Sn(OH)_4\ ;\ \ SnCl_4 + 2HCl \rightarrow H_2[SnCl_6]$$

17.6.16. Stannous and Stannic Oxides. Addition of alkali to tin (II) solution first precipitates hydrated stannous oxide. This dissolves in excess alkali to give stannite ion:

$$Sn(OH)_2 + OH^- \rightarrow HSnO_2^- + H_2O$$

The stannite ion is a strong reducing agent as is indicated by its redox potential: $[Sn(OH)_6]^{4-} \rightleftharpoons HSnO_2^- + 3OH^- + H_2O; E^\circ = -0.9$ volt. It reduces permanganate to manganese dioxide:

$$2MnO_4^- + 3SnO_2^{2-} + H_2O \rightarrow 2MnO_2 + 3SnO_3^{2-} + 2OH^-$$

It also reduces a bismuth (III) compound to black metallic bismuth.

Tin dioxide occurs in nature. Hydrated tin dioxide called metastannic acid (or β-stannic acid) is obtained by the action of concentrated HNO_3 on metallic tin:

$$Sn + 4HNO_3 + (x-2)H_2O \rightarrow SnO_2.xH_2O + 4NO_2$$

This variety of hydrated tin dioxide dissolves in alkali but not in acids. The α-stannic acid is obtained by the acidification of aqueous solutions of alkali metal stannates. This form is readily soluble in acids to form stannic compounds and in alkali to form alkali stannates. Crystalline alkali stannates such as $K_2SnO_3.3H_2O$ really contain the anions $[Sn(OH)_6]^{2-}$. Six OH^- groups surround tin (IV) octahedrally. Both forms of the hydrated oxide have the same crystal structure. The difference in their reactivity is due to a difference in particle sizes and in the nature of the surfaces of the particles.

17.6.17. Mosaic Gold : Hydrogen sulphide precipitates from a dilute acid solution of stannic compounds a yellow precipitate of stannic sulphide SnS_2. On a technical scale stannic sulphide is prepared in the form of golden yellow scales by heating metallic tin, mercury (or tin amalgam), flowers of sulphur and ammonium chloride. This product is used as a pigment under the name *mosaic gold* (gold for mosaic work) and under the name *tin bronze* for bronzing.

17.6.18. Tetraalkyl Lead : Tetraethyl and tetramethyl lead are commercially the most important organolead (with carbon-lead bond) compounds. They can be made by the action of alkyl halides on sodium-lead alloy or by the electrolysis of alkyl magnesium halides with a lead anode. The lead anode is attacked by the alkyl anions or radicals to give lead tetraalkyls. Tetraethyl lead is made by the action of ethyl chloride on an alloy of lead with 10% sodium, pyridine being used as a catalyst. A temperature of 40—60°C is usually maintained. The tetraethyl lead is separated by steam distillation:

$$4C_2H_5Cl + 4NaPb \rightarrow Pb(C_2H_5)_4 + 4NaCl + 3Pb$$

The alkylleads are viscous toxic liquids and are used as antiknock agents in gasoline. A small percentage of tetraethyl lead in petrol can prevent 'knocking' in an engine, whereby it is possible to have a higher compression in the cylinders and hence a higher efficiency. About 2—3 ml of lead tetraethyl is used per gallon of petrol.

17.6.19. Lead Tetraacetate : This is one of the strongest oxidants known, the formal redox potential in perchloric acid being ~ + 1.6 volt. It oxidises cobalt (II) to cobalt (III), manganese (II) to manganese (III), cerium (III) to cerium (IV) but lead (II) cannot be oxidised. Chloride, bromide and iodide are oxidised to the respective halogens. It is a useful oxidant in organic syntheses. Alcohols are oxidised to aldehydes. It has also been used as a methylating agent.

Reaction of red lead oxide with glacial acetic acid at 60°C gives both lead (II) and lead (IV) acetate. Acetic anhydride is added to suppress hydrolysis of the tetraacetate by arresting the liberated water.

$$Pb_3O_4 + 8CH_3COOH \rightarrow Pb(CH_3COO)_4 + 2Pb(CH_3COO)_2 + 4H_2O$$

$$Pb(CH_3COO)_4 + 2H_2O \rightarrow PbO_2 + 4CH_3COOH$$

Because of its insolubility in glacial acetic acid, lead dioxide cannot be used as a substitute for Pb_3O_4. 95% yield of lead tetraacetate has been claimed by the electrolysis of lead (II) acetate in anhydrous acetic acid. The tetraacetate crystallises at platinum anode at ~ 80°C.

17.6.20. White Lead : Basic lead carbonate $2PbCO_3.Pb(OH)_2$ is an important white pigment called white lead. Alkali carbonates also precipitate a basic lead carbonate of the same composition but this variety is useless as a pigment since it is crystalline and has a poor covering property. White lead is commercially made by the action of air, CO_2 and acetic acid on lead metal. In the presence of air and acetic acid the lead is oxidised to a basic lead acetate which reacts with CO_2 and H_2O to give the basic carbonate. Rolls of sheet lead are placed in earthenware pots over dilute acetic acid. The pots are loosely covered with barks. The fermentation of the barks provides the necessary warmth, and give CO_2 which is essential for the reaction:

$$2Pb + 2CH_3COOH + O_2 \rightarrow 2Pb(OH)(CH_3COO)$$

$$3Pb(OH)(CH_3COO) + 2CO_2 + H_2O \rightarrow Pb(OH)_2.2PbCO_3 + 3CH_3COOH$$

White lead mixed with linseed oil makes a good white paint. It is, however, darkened in city atmosphere due to H_2S.

17.6.21. Red Lead : It is made by heating (~ 350°C) lead monoxide in a current of air in a muffle furnace:

$$6PbO + O_2 \rightleftharpoons 2Pb_3O_4$$

Higher temperature favours the backward reaction. It is a brilliant red powder. With HCl it gives $PbCl_2$ and Cl_2:

$$Pb_3O_4 + 8HCl \rightarrow 3PbCl_2 + 4H_2O + Cl_2$$

It is used as a red pigment.

17.6.22. Lead Dioxide : This is made by oxidising an alkaline solution of a lead salt by chlorine:

$$PbCl_2 + NaOCl + 2NaOH \rightarrow PbO_2 + 3NaCl + H_2O$$

Lead acetate solution also reacts with bleaching powder on steam bath to give PbO_2. The product is digested with hot dilute HNO_3 to remove any bleaching powder. Pb_3O_4 may also be oxidised by dilute HNO_3 to PbO_2:

$$Pb_3O_4 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$

Lead dioxide is a strong oxidant:

$$2MnSO_4 + 5PbO_2 + 6HNO_3 \rightarrow 2HMnO_4 + 2PbSO_4 + 3Pb(NO_3)_2 + 2H_2O$$

$$2Cr(OH)_3 + 10KOH + 3PbO_2 \rightarrow 2K_2CrO_4 + 3K_2PbO_2 + 8H_2O$$

17.7. ISOLATION OF THE GROUP IVB ELEMENTS

17.7.1. Silicon. *Silica* and *silicate* materials are the vast sources of silicon. Silicon can be obtained by heating silica with magnesium powder, carbon or aluminium powder in thermite process:

$$SiO_2 + 2Mg \rightarrow Si + 2MgO \ ; \ SiO_2 + C \rightarrow Si + 2CO$$

$$2SiO_2 + 4Al \rightarrow 3Si + 2Al_2O_3$$

Extrapure silicon is obtained by a large number of steps. The ordinary commercial silicon, as obtained above, is changed to a silicon halide and this halide is freed from impurities like boron halides, arsenic halides by fractional distillation. The silicon halide is then reduced by hydrogen in a heated tube. Final purification is done by *zone melting*, which is simple in principle but is a formidable task in practice. A rod of an impure element is heated at one end such that a small cross sectional area gets fused. Impurities in general are more soluble in a melt than in a solid. The heat source is gradually moved along the impure rod, thus making the impurities collect at the lower end of the rod. The impure lower end is then cut off leaving behind a rod of extrapure silicon.

17.7.2 Germanium. Germanium ores are very rare. An important natural source is *germanite*, a copper iron thiogermanate $Cu^{I}_5(Cu^{II}, Fe^{II})_6 As^{III}Ge^{IV}S^{II}_{12}$. The ore is attacked with nitric acid – sulphuric acid mixture. Most of the germanium separates as GeO_2. This is dissolved in dilute HCl and $GeCl_4$ distilled out. The distillate is received in water when pure GeO_2 separates. It is reduced to the metal by hydrogen or by carbon.

17.3.3. Tin : Tin occurs in nature mostly in the form of *cassiterite* or *tinstone*, SnO_2. The percentage of tin dioxide in this mineral may not exceed 10%, being overburdened with silicate materials, iron pyrites, arsenical pyrites etc. The ore is crushed and concentrated by a shaking device making use of a density difference. Heavy cassiterite is thus freed from lighter silicate materials but is still contaminated with heavy *wolframite* ($FeWO_4 + MnWO_4$), *iron pyrites* FeS_2 and *mispickel* FeSAs. The ore is then treated in an electromagnetic separator when most of the iron-containing ore is separated from cassiterite. The ore is then roasted in a current of air to remove sulphur and arsenic as oxide vapours. Remaining tin dioxide is mixed with anthracite coal and some lime and fluorspar (to form a slag) and smelted in a reverberatory furnace:

$$SnO_2 + 2C \rightarrow Sn + 2CO$$

The slag contains much tin and is worked up by smelting in a blast furnace with coke. The material still contain impurities like iron. This is further purified by melting the crude metal and allowing the pure metal to flow away leaving an alloy of tin with copper, iron and arsenic.

17.7.4. Lead : The metal occurs chiefly as *galena* PbS, the less important sources being *cerussite* $PbCO_3$ and *anglesite* $PbSO_4$. The ore is concentrated from ~ 8% to ~ 60% galena by a froth floatation process. It is then mixed with some lime (to serve as a flux) and roasted in a blast of air. The gases produced are sucked away. During the operation galena is converted to PbO:

$$2PbS + 3O_2 \rightleftharpoons 2PbO + 2SO_2$$

The roasted material is then mixed with coke (to serve as a fuel and reducing agent) and a flux (iron oxide + lime) and treated in a blast furnace where the following reactions occur:

$$PbO + C \rightarrow Pb + CO \; ; \; 2PbO + PbS \rightarrow 3Pb + SO_2$$

$$2PbS + Fe_2O_3 + 3C \rightarrow 2FeS + 2Pb + 3CO$$

The metallic lead collects at the bottom and is removed. The slag consisting of calcium silicate and iron sulphide are drawn off through the slag hole at the bottom of the furnace. The crude lead is purified by an electrolytic process. Impure lead is cast into rods to serve as anodes in an electrolytic cell. Sheets of pure lead are used as cathode and a solution of $PbSiF_6$ serves as an electrolyte. The electrolyte is prepared by the action of H_2SiF_6 on lead. For this purpose fluorspar, CaF_2, is first heated with H_2SO_4 and the liberated HF is absorbed in an aqueous suspension of crushed silica:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF \; ; \; 6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O$$

The H_2SiF_6 solution is next passed into a box containing granulated lead or white lead where $PbSiF_6$ is formed:

$$3H_2SiF_6 + Pb(OH)_2.2PbCO_3 \rightarrow 3PbSiF_6 + 4H_2O + 2CO_2$$

The final electrolyte contains ~17% $PbSiF_6$ and 3—9% H_2SiF_6. Concrete or wooden tanks are used as electrolytic vessels. Optimum temperature is 35—40°C. Impurities like copper, antimony, arsenic, bismuth, silver and gold are thrown down as anode mud while the more electropositive metals (eg: iron) are retained in solution.

17.8. USES OF THE GROUP IVB ELEMENTS

Silicon and *germanium* are finding many uses as semiconductors, particularly in transistors. Transistors serve a purpose similar to the electronic vacuum tubes.

A major industrial use of *tin* is the manufacture of tin plates (steel plates coated with tin) which are used chiefly as containers of food. Sheet steel coated with a lead-tin alloy is used for roofing and for gasoline tanks. Tin is also an important constituent of *solders* (~50% Sn, ~50% Pb), *brasses* (copper and tin as major constituents). For details see Chapter 29.

Lead is used in the manufacture of lead storage batteries and also white lead and other pigments. The metal is also incorporated in many alloys: *solder* (~ 50% Sn, ~ 50% Pb) and *type metals* (70—85% Pb, 30—15% Sb). Because of their low melting points and because of their expansion on solidification lead-antimony alloys serve as type metals and produce sharp outlines.

The reactions involved in lead storage battery have been discussed in Part I, page 142.

17.9. ANALYTICAL REACTIONS OF THE GROUP IVB ELEMENTS

Carbon content of organic compounds is determined by combustion with copper oxide in an atmosphere of oxygen. The CO_2 formed is absorbed in alkali and weighed. Carbonates are readily detected by the effervescence produced on the addition of dilute acids. The usual practice of decomposing organic compounds is to fume with concentrated H_2SO_4 whereby carbon is removed as CO_2.

Silicon is determined gravimetrically as SiO_2. In qualitative detection a silicon compound is treated with HF whereby volatile SiF_4 is produced, which gives turbidity in water due to the formation of silicic acid and silica:

$$SiO_2 + 4HF \rightleftharpoons SiF_4 + 2H_2O \; ; \; 3SiF_4 + 2H_2O \rightarrow SiO_2 + 2H_2SiF_6$$

Colourless *germanium disulphide* is precipitated by H_2S from strongly acid solution. The disulphide is soluble in ammonium sulphide giving thiogermanates:

$$GeS_2 + (NH_4)_2S \rightarrow (NH_4)_2\,[GeS_3]$$

The sulphide can be ignited to the dioxide and weighed.

Tin belongs to group IIB of the qualitative scheme of analysis. SnS is brown and SnS_2 is yellow. Both the sulphides are precipitated by H_2S from not too strongly acid solutions. The sulphides dissolve in ammonium *polysulphide* solution producing thiostannates:

$$SnS_2 + 2(NH_4)_2S \rightarrow (NH_4)_4[SnS_4] \; ; \; SnS_2 + (NH_4)_2S \rightarrow (NH_4)_2[SnS_3]$$

$$SnS + S + (NH_4)_2S \rightarrow (NH_4)_2[SnS_3]$$

Tin (II) salts are often detected by their reaction towards mercuric chloride, when insoluble Hg_2Cl_2 is precipitated. For quantitative estimation tin (in alloys) is precipitated by nitric acid as metastannic acid, $SnO_2.xH_2O$, (17.6.14). The metastannic acid is ignited to SnO_2. Some impurities accompany the tin dioxide. The error in weighing the impure SnO_2 can be eliminated by heating the dioxide with pure NH_4I when tin dioxide volatilises as SnI_4:

$$SnO_2 + 4NH_4I \rightarrow SnI_4 + 4NH_3 + 2H_2O$$

The loss in weight gives the correct weight of SnO_2.

Sparing solubility of $PbCl_2$ includes *lead* in group I of the qualitative scheme. Its sulphide is also precipitated in acid solution so that it is also included in group IIA of the scheme. Quantitatively it is estimated as insoluble $PbSO_4$ or $PbCrO_4$.

STUDY QUESTIONS

1. The elements of group IVB show + 2 and + 4 oxidation states and yet these are not transition elements. Explain.

2. The tetrahalides of group IVB elements are covalent but not ionic. Comment.

3. The oxides of + 2 tin and + 2 lead are more basic and less acidic than the corresponding oxides of + 4 tin and + 4 lead. Elucidate.

4. $SiCl_4$ and CCl_4 are both tetrahedral and use similar hybrid orbitals. $SiCl_4$ is readily hydrolysed but not CCl_4. Explain.

5. Give an account of the varieties of hybridisations in carbon and silicon compounds.

6. Diamond is extremely high melting but is a non-conductor. Graphite is covalent but is a conductor. Both are basically the same element. How do you correlate these facts ?

7. Metallic properties increase from carbon to lead. Justify.

8. Extreme inertness of fluorocarbons (e.g. CF_4, C_nF_{2n+2}) has been explained on the following lines: (*a*) neither carbon nor fluorine has *d*-orbitals (*b*) neither carbon nor fluorine can expand its octet (*c*) fluorine atoms effectively shield the carbon atoms (*d*) in C-F bonds carbon may be supposed to have undergone oxidation (whereas in C–H it may be assumed to have been reduced) so that fluorocarbons are not susceptible to oxygen or air. Present a connected picture.

9. Discuss the reasons leading to differences between carbon and silicon.

10. Give a concise account of the general trends in the properties of group IVB elements.

11. If CO can act as a good ligand for low oxidation states of metals why can't CO_2 or SiO_2 ? (consult also Chapter 23).

12. Sketch the extraction procedures for tin and lead and mention some of their industrial uses.

13. Write short accounts of (*a*) lead tetraacetate (*b*) silicones (*c*) freons (*d*) synthetic zeolites and molecular sieves.

14. Starting with the electronic configurations enumerate the behaviours of the hydrides and halides of group IVB elements.

15. A number of silicon hydrides analogous to paraffin hydrocarbons are known but there are as yet no reports for silicon analogues of olefines, acetylenes or aromatics. Discuss.

16. Bipositive tin can function both as a donor and also as an acceptor. Explain.

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18

Group VB Nitrogen, Phosphorus, Arsenic, Antimony and Bismuth

Nitrogen occurs in our atmosphere to the extent of 78% by volume. Sodium nitrate (chile saltpetre) is about the only inorganic nitrogenous compound that is found in nature in large amount. This element is essential for living organisms where it is present as a constituent of proteins and albumins. Phosphorus occurs mainly as calcium phosphate. Arsenic, antimony and bismuth occur mainly as sulphides: $FcAsS$, Sb_2S_3 and Bi_2S_3. The relative abundances in the earth's crust are: N(0.005%); P(0.11%); As (5×10^{-4}%); Sb(5×10^{-5}%) and Bi ($\sim 10^{-5}$%).

18.1. COMPARATIVE STUDY OF THE GROUP VB ELEMENTS

18.1.1. General Considerations : The outer quantum shell electronic configuration of the elements is s^2p^3 with two paired electrons in the *s*-orbital and one unpaired electron each in the three *p*-orbitals. The electronic configurations (Table 18.1) suggest that the elements are closer to the next noble gas than to the preceding noble gases. Their assuming the + 5 cationic configurations by losing all the five outer electrons is just impossible. The huge amount of energy necessary for the purpose, as evidenced from the sum of the five ionisation potentials, cannot be compensated by gain of lattice energy by the ionic crystal. Therefore all their compounds in formal group valence are covalent. The first ionisation potential gradually falls from nitrogen to bismuth indicating a slow but steady rise in metallic character. In trivalent state (*inert pair effect*) also, metal (cationic) character becomes prominent in the heavier elements; nitrogen and phosphorus being wholly acidic (non-metallic), arsenic and antimony amphoteric and bismuth predominantly basic (metallic). The trend in the group is from a purely non-metallic nitrogen chemistry to a metallic chemistry in bismuth. Arsenic and antimony exhibit intermediate properties and hence they are often termed as metalloids.

Table 18.1. Electronic Configurations and Some Properties of Group VB Elements

Element	Atomic Number	Electronic Configuration	Ionisation Potential (*ev*)	Electro-negativity
Nitrogen	7	[He] $2s^22p^3$	14.53, 29.59, 47.42, 77.45, 97.86	3.0
Phosphorus	15	[Ne] $3s^23p^3$	10.48, 19.72, 30.15, 51.35 65.00	2.1
Arsenic	33	[Ar] $3d^{10}4s^24p^3$	9.81, 18.63, 28.34, 50.1 62.6	2.0
Antimony	51	[Kr] $4d^{10}5s^25p^3$	8.64, 16.5, 25.3, 44.1, 56	1.9
Bismuth	83	[Xe] $4f^{14}5d^{10}6s^26p^3$	7.29, 16.68, 25.56, 45.3, 56.0	1.9

In keeping with general group trends the electronegativities fall down the group. Note that the electronegativity of nitrogen is quite high being exceeded only by oxygen and fluorine. The falling electronegativity down the group makes the bonds of the heavier elements of this group with highly electronegative elements like oxygen, chlorine and fluorine predominantly polar. Recall the rule that the larger the electronegativity difference between the combining atoms the larger is the per cent ionic character (Chapter 4). Thus BiF_3 is an ionic compound and many other bismuth (III) compounds exist as salts of the oxocation BiO^+. Some antimony compounds also have SbO^+ ions.

An interesting exercise in this group is to study the many ways the elements, particularly nitrogen, can attain the next noble gas electronic configuration: (1) One way to achieve this is to acquire three electrons straightaway, forming trivalent anions. This is realised best in nitrogen (eg: in alkali nitrides) but less readily in the heavier members because of their lower electron affinities and lower electronegativities. (2) Octet can also be achieved through the formation of three single covalent bonds. In such cases a lone pair is available for coordination to metal ions or to Lewis acids. Widely varying electronegativities undoubtedly influence the properties of such tricovalent compounds—for example, NH_3 is a base, PH_3 is neutral and the other hydrides may even be slightly acidic. (3) Octet may also be realised by gaining one electron and forming two single bonds as in the amide (NH_2^-), or by gaining two electrons and forming one covalent bond as in the imide (NH^{2-}) ions. Note that such ions have two or three lone pairs so that they are capable of working as bridging ligands between two coordination centres.

Nitrogen alone does not possess any potential *d*-orbital since $n = 2$ shell can have none. This makes a lot of difference in the chemistry of the group VB elements. Whereas phosphorus and all the other elements can expand their valence shell to accommodate electrons beyond an octet, nitrogen cannot. Thus nitrogen halides are restricted upto only the trihalides but phosphorus has pentahalides in addition to the trihalides. Through the agency of *d*-orbitals phosphorus can utilise all its five valence electrons to form pentacovalent trigonal bipyramidal PCl_5 (sp^3d-hybridisation). By virtue of the *d*-orbitals such halo anions $[BiCl_6]^{3-}$, $[SbCl_6]^{3-}$ (sp^3d^2 hybridisation) also exist.

Expectedly single bond covalent (atomic) radius and tripositive cationic radius (Table 18.2) increase down the group. Compared to phosphorus the increase in bismuth is substantial so that according to Fajans' rules if any metallic character is to appear in the group it is best possible in Bi^{3+}. Increasing metal character generally should be reflected in increasingly more negative standard potentials. Unfortunately the potentials are positive and low. The effect of decreasing ionisation potential is apparently offset by reduced heats of hydration (also see Chapter 20).

Table 18.2. Some More Properties of Group VB Elements

Element	Atomic Radius (A)	Ionic Radius (M^{3+},A)	M.P. (°C)	B.P. (°C)	Density (*g/ml*)	$E°$, volts $M^{3+} + 3e \rightleftharpoons M$
Nitrogen	0.70	...	−210	−196	1.027	...
Phosphorus	1.06	0.34	44	287	1.83	...
Arsenic	1.19	0.69	817 (36 atm.)	616	5.7	+ 0.25
Antimony	1.38	0.90	630	1440	6.6	+ 0.21
Bismuth	1.46	1.20	271	1420	9.8	+ 0.32

18.1.2. Chemical Behaviour. *Hydrides*: All the elements form volatile, covalent hydrides XH_3. The H-N-H bond angle is ~107° with sp^3 hybridisation of nitrogen orbitals whereas in the other hydrides the bond angles are close to ~90° indicating the use of either pure '*p*' orbitals for overlap or a very effective repulsion by the valence shell electron pairs of the tetrahedral sp^3 hybrid orbitals of the central atom (Chapter 6). The hydrides can all be obtained by a general method of hydrolysis of metal nitride, phosphide, arsenide etc. The thermal stability of the hydrides decreases rapidly with increasing atomic weight of the parent element, and these hydrides appear to be less stable than the hydrides of group IV or of group VI. Compare the bond dissociation energies (Kcal/mole): N-H, 93; P-H, 76; As-H, 59 and Sb-H, 61. The falling thermal stability with increasing atomic size of the parent element may be traced to the greater X-H distance leading to a weakening of the covalent bond. In spite of the greater electronegativity of nitrogen, ammonia is much the strongest electron donor among the hydrides of this group. The explanation must lie in the small size of the nitrogen atom and consequently a higher electron density in its smaller sp^3 hybrid orbital compared to phosphorus and other elements. Ammonia behaves as a base forming NH_4^+. Phosphine is a much weaker donor, PH_4Cl and PH_4Br being unstable in water. In arsenic hydride no tendency to coordinate is noticed and no stable salts of the arsonium AsH_4^+ ion are known. In keeping with their decreasing tendency to accept a proton in aqueous solution, the solubility of the hydrides in water falls down the series. The reducing ability of the hydrides increases down the group, the higher members being stronger reducing agents. A final point is the extensive association of ammonia due to the larger electronegativity of nitrogen (Chapter 5). A summary of the general property trends of the XH_3 hydrides is given below (Table 18.3).

Table 18.3. Comparative Study of the Group VB Hydrides

Property	NH_3	PH_3	AsH_3	SbH_3	BiH_3
General method of synthesis	Acid hydrolysis of M^{I}_3X($X = N,P,As,Sb,Bi$) →				
Thermal stability	Decreases →				
Reducing ability	Increases →				
Association and hydrogen bonding	Decreases →				
Base strength	Decreases →				
Donor ability	Decreases →				

Halides: With the exception of NBr_3 and NI_3 all the trihalides are known. As expected BiF_3 and to some extent SbF_3 are ionic, all others being covalent. The covalent halides have tetrahedral (sp^3 hybridised) structures with a lone pair of electrons residing in the fourth orbital. Interesting difference is observed in the behaviour of NF_3 and NCl_3 towards water. Whereas NCl_3 is readily hydrolysed NF_3 is not. This is because in NF_3 neither nitrogen nor fluorine can accommodate a lone pair of H_2O molecule since they do not possess any vacant *d*-orbital to assist in the nucleophilic attack (by H_2O) prior to hydrolysis. But chlorine in NCl_3 does possess *d*-orbitals to facilitate such attack by H_2O:

$$NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$$

The nature of the product (HOCl) points to such a mechanism. Since P, As and Sb can all expand their valence shell, their trihalides are readily hydrolysed:

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

$BiCl_3$ and $BiBr_3$ are more ionic and hydrolyse to give BiO^+ but not Bi^{3+}. Interestingly due to the extreme electronegativity of fluorine NF_3 is a poor donor as against the moderate donor ability of the phosphorus trihalides. A sufficiently powerful electron acceptor, BF_3, alone can force NF_3 to coordinate: $F_3N \rightarrow BF_3$.

Since nitrogen has no *d*-orbitals it cannot form pentahalides but the other elements can. The pentahalides have a trigonal bipyramidal structure with valence shell of $5 + 5 = 10$ electrons of the central element (sp^3d hybridisation). The valence shell expansion to a shell of 12 occurs in the octahedral complexes $[PCl_6]^-$, $[AsF_6]^-$ etc with sp^3d^2 hybridisation. PF_5 is a very strong Lewis acid forming complexes with amines, ethers and other bases giving 6-coordinate octahedral compounds.

Oxides: Nitrogen forms the largest number of oxides with oxidation numbers + 1, + 2, + 3, + 4 and + 5. Phosphorus, arsenic, antimony form oxides in the + 3 and + 5 states and bismuth oxide is known only in the + 3 state (Table 18.4). While the oxides of nitrogen, phosphorus and arsenic are acidic, those of antimony are amphoteric while bismuth trioxide is basic. Most nitrogen oxides are monomers and a limited few dimerise under special conditions. The phosphorus oxides are based on the tetrahedral P_4 skeleton. The As_4O_6 and Sb_4O_6 molecules are also based on the tetrahedral As_4 and Sb_4 skeletons. The structures of the As_2O_5 and Sb_2O_5 are not known. The yellow bismuth trioxide is soluble in acids to give bismuth (III) salts but possesses no acidic character since it is insoluble in alkalies. Two important generalisations can be made: (*a*) In a given oxidation state the basic character of the oxides increases down the group (*b*) Oxides with increasing atomic number, and with increasing oxidation number of the parent element become more acidic and less stable. This point is exemplified by the absence of the oxide Bi_2O_5. Although Bi_2O_5 is unknown, it must be acidic since bismuthates ($NaBiO_3$) derived from the hypothetical Bi_2O_5, are known.

Table 18.4. Oxides of Group VB Elements

Element	Oxidation Number +1	+2	+3	+4	+5
Nitrogen	N_2O	NO	N_2O_3	NO_2, N_2O_4	N_2O_5
Phosphorus			P_4O_6		P_4O_{10}
Arsenic			As_4O_6		As_2O_5
Antimony			Sb_4O_6		Sb_2O_5
Bismuth			Bi_2O_3		

Acidity increases/stability decreases →

Basic character increases ↓

Oxyacids: Following the electronegativity-acidity rule (Chapter 8) oxyacids with higher oxidation numbers are strong acids. This is particularly noted in the oxyacids of nitrogen and to a lesser degree in oxyacids of phosphorus. Oxyacids with lower oxidation numbers are in most cases strong reducing agents and those with the higher oxidation numbers are oxidants. Phosphorus acids show some special property of forming a number of condensed phosphates, many of which have found industrial and analytical applications. A point of interest arises in the composition of the acids of this group. Whereas phosphoric (H_3PO_4) and arsenic acids (H_3AsO_4) are based on a tetrahedral skeleton (sp^3 hybridisation), antimonic acid is octahedral in the $[Sb(OH)_6]^-$ form. Salts of antimonic acid, of the form $M^{I}SbO_3$, $M^{III}SbO_4$ may be regarded as mixed oxides where Sb is octahedrally surrounded by six oxide ions. Ability of antimony to accommodate six OH^- or O^{2-} groups around itself is due to its larger size. Similar reasoning holds for telluric acid (Chapter 19). Stable oxyacid salts of bismuth (III) can be crystallised from moderately strong acid solutions eg: $Bi(NO_3)_3.5H_2O$, $Bi_2(SO_4)_3$ etc. $Bi(OH)_3$ behaves as a metallic hydroxide giving a whole series of salts such as nitrate, sulphate, perchlorate. A summary of the oxyacids of this group is given in Table 18.5.

Table 18.5. Oxyacids of Group VB Elements

Element	Oxidation Number	Oxyacid and Salts	Strength of the oxyacids in water
Nitrogen	+ 1	$H_2N_2O_2$ (hyponitrous acid) is known as white crystals. Salts such as $Ag_2N_2O_2$ are known.	$K_A \sim 10^{-7}$; weak acid
	+ 3	HNO_2 (nitrous acid) is known only in solution. Salts such as $NaNO_2$ are known.	$K_A \sim 10^{-6}$; weak acid
	+ 5	HNO_3 (nitric acid) is known. Salts such as $NaNO_3$ are well known. HNO_3 is a strong oxidant.	K_A is very large; very strong acid
Phosphorous	+ 1	H_3PO_2 (hypophosphorous acid, better written as $H[H_2PO_2]$ is known only in solution. Salts are known. Acid and the salts are strong reducing agents.	monobasic acid; $K^I \sim 10^{-2}$; weak acid
	+ 3	H_3PO_3 phosphorous acid, better written as $H_2[HPO_3]$) is known as crystals, M. P., ~70°C; mild reducing agent.	dibasic acid; $K_A^I \sim 10^{-2}$; weak acid
	+ 4	$H_4P_2O_6$(hypophosphoric acid) is known as a dihydrate. It is a tetrabasic acid, although salts of the type $Na_2H_2P_2O_6$ are only known.	$K_A^{I} \sim 10^{-3}$; $K_A^{II} \sim 10^{-3}$; $K_A^{III} \sim 10^{-8}$; $K_A^{IV} \sim 10^{-10}$
	+ 5	H_3PO_4 (phosphoric acid) is known as low melting (M.P. ~ 43°C) solid. A variety of salts are known; many of the salts are condensed polyphosphates; no oxidising or reducing property.	$K_A^{I} \sim 10^{-2}$; $K_A^{II} \sim 10^{-6}$; $K_A^{III} \sim 10^{-12}$ weak acid

Element	Oxidation Number	Oxyacid and Salts	Strength of the oxyacids in water
Arsenic	+ 3	$HAsO_2$ or H_3AsO_3 (arsenious acid) is known only in solution. Salts are known. The acid is readily oxidised in solution.	
	+ 5	H_3AsO_4(arsenic acid)is known in solution. It is an oxidant. It is a weak tribasic acid. Condensed arsenates are unstable.	K_A^I 10^{-2}; weak acid
Antimony	+ 3	$H_3[Sb(OH)_6]$ (antimonous acid) is known only in solution.	
	+ 5	Antimonates (salts of the hypothetical antimonic acid) are of the types: M^ISbO_3, $M^{III}SbO_4$, $M^{II}_2Sb_2O_7$. $[Sb(OH)_6]^-$ crystallises with large cations such as $[Co(NH_3)_6][Sb(OH)_6]_3$	
Bismuth	+ 3	Lower acid and salts are unknown.	
	+ 5	Salts of the higher acid (such as $NaBiO_3$) are known. Bismuthates are strong oxidants.	

Donor-Acceptor Properties. This is the first group in the Periodic Table where we meet elements, some of whose compounds are the most formidable coordinating ligands. In group IV, the four-covalent compounds are devoid of lone pairs and hence cannot serve as ligands. CO, an electron deficient compound, in the + 2 state, however, can serve as a ligand. In group V, the tricovalent compounds have a lone pair of electrons. The lone pair empowers the tricovalent compounds of N, P, As to function as donors. This donor ability falls off down the group. Practically no ligand properties are known with bismuth (III) and antimony (III).

From SHAB theory (Chapter 8) it follows that for hard acid metal ions (class 'a' acceptors) the donor ability of the ligand atoms will have the sequence: $N > P > As > Sb > Bi$. For soft acid metal ions (class 'b' acceptors) the sequence becomes: $N < P > As > Sb > Bi$. Not all trivalent nitrogen and trivalent phosphorus compounds will be equally effective as donors. For example, introduction of electron withdrawing group will reduce the donor strength. PF_3 is a weaker donor than PCl_3.

Because of the availability of empty *d*-orbitals P(III)/As(III) ligands are capable of stabilising low oxidation states (by receiving back donated electrons from low-valent metals to their *d*-orbitals) whereas nitrogen cannot do so (Chapter 23).

18.2. ELEMENTARY FORMS OF THE GROUP VB ELEMENTS

Nitrogen forms diatomic molecule N_2 whereas phosphorus, arsenic and antimony form tetraatomic molecules P_4, As_4, Sb_4. Structure determination shows that in N_2 the N — N distance is far too short (1.09A) as compared to N — N single bond (1.5A) and N = N double bond (1.2A). A triple bond is thus indicated in N_2 molecule. Taking *x* axis as the bond axis the two p_x orbitals of each nitrogen with one unpaired spin on each overlap giving a $p_x - p_x$ sigma bond. Then p_y and p_y orbitals with one unpaired spin on each overlap to make one π-bond. Similarly the overlap of the p_z orbitals gives the second π-bond (Fig. 18.1). A lone pair of electrons remains on the *s*-orbital of each nitrogen. Instead of pure $p_x - p_x$ orbital overlap we may also invoke $s - p_x$ hybridisation of each nitrogen giving two equivalent *sp* hybrid orbitals and then put two electrons in one *sp* hybrid (forming the lone pair), one electron in the other *sp* hybrid and one unpaired spin each in the p_y and p_z orbitals. Then the *sp* hybrids of the two nitrogen atoms with one unpaired spin on each will overlap to give *sp*—*sp* sigma bond. The other two *p*-orbitals will overlap to give two π-orbitals. Note that the triple bond also follows on the molecular orbital model (Chapter 5). In diatomic O_2 molecule there is effectively a double bond (both on the VB and the MO model, Chapter 5) and in F_2 there is a single bond. Interestingly as the multiplicity of the bond decreases from N_2 through O_2 to F_2 the bond strength decreases along the period:

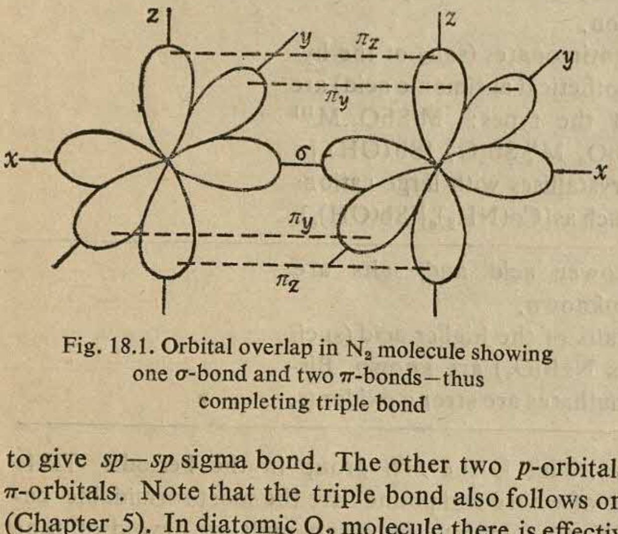


Fig. 18.1. Orbital overlap in N_2 molecule showing one σ-bond and two π-bonds—thus completing triple bond

Molecule	N_2	O_2	F_2
Internuclear Distance (A)	1.09	1.21	1.42
Bond Energy (Kcal/mole)	225	118	38

The strength of the triple bond in N_2 makes the molecule extremely inert. Although the triple bond is so strong, N—N single bond is comparatively weak. Compare the single bond energies in H_3C-CH_3, H_2N-NH_2, H—O—O—H and F—F: C—C, 83; N—N, 38; O—O, 33 and F—F, 38 Kcal/mole. There is a sudden drop from carbon to nitrogen, being due to repulsive interaction between the lone pairs of the two tetrahedral nitrogens of hydrazine. The lone pair repulsion model should explain why we do not find a non-ending polymeric graphite-like layer structure of nitrogen with sp^2 hybridisation with each nitrogen being linked by single bonds to three other nitrogens in the same plane. Interestingly the non-ending polymeric sp^2 structure obtains in black phosphorus in a distorted form.

As we move down the group the strength of the multiple bonding among the same two elements becomes weak due to enhanced size of the orbitals (compare Si). Therefore the octet is realised in yet another way by forming tetrameric tetrahedral molecules. In P_4 the four phosphorus atoms are sitting at the four corners of a tetrahedron (Fig. 18.2). The angles P–P–P are all 60°. Ideally pure *p-p* overlap should make the P–P–P bond angles 90° and hence the actual structure must be quite strained. This tetrahedral P_4 form is present in white phosphorus. The strained P_4 molecule is responsible for the reactivity of white phosphorus. This is stored under water to prevent oxidation by air. White phosphorus at ~ 250°C gives red P (structure not definitely established), and under high pressure and temperature gives a black variety which has a complicated polymeric sheet structure. Each atom in black phosphorus is linked to three near neighbours (sp^2 hybridisation) in a sheet. In between the sheets there is a weak van der Waals' attraction.

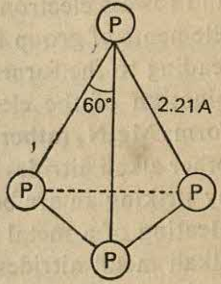


Fig. 18.2. P_4 molecule

Ordinary stable forms of As, Sb and Bi are bright, metallic in lustre and have structures comparable to black phosphorus. Unstable, tetrahedral As_4, Sb_4 are obtained by rapid condensation of vapours, and are very reactive.

18.3. ACTIVE NITROGEN

Passage of electric discharge through molecular nitrogen produces an active variety of nitrogen. It is now agreed that active nitrogen is made of nitrogen atoms. It affords some very unusual reactions, for example, with hydrocarbons it produces HCN presumably by an attack on the carbon. It reacts with mercury at room temperature to form a nitride. It combines readily with phosphorus, sulphur, iodine to give their nitrides—reactions which are not shown by ordinary molecular nitrogen.

It reacts with H_2S to give a blue solid believed to be sulphur nitride $(NS)_x$. CS_2 reacts with active nitrogen to give $(NS)_x$ and $(CS)_x$. The nitrogen atoms recombine with a yellow afterglow which persists for some period after switching off the electric discharge.

It is believed that active nitrogen is really atomic nitrogen with three unpaired electrons i.e. $1s^2\,2s^2\,2p_x^1\,2p_y^1\,2p_z^1$. Two such atoms combine to give an excited $:\dot{N}-\dot{N}:$ molecule with four unpaired electrons, which then rearrange to the diamagnetic $:N \equiv N:$.

18.4. BINARY NITRIDES

Binary nitrides can be classified, just as we did for binary hydrides and carbides, into three classes: I. Salt like nitrides, II. Covalent nitrides, and III. Interstitial or transition metal nitrides.

.**18.4.1. Saltlike Nitrides:** We noted in the beginning of this Chapter that one straightforward way of achieving the octet in nitrogen is by gaining three electrons. It is a simple guess now that elements which have the lowest ionisation potentials and lowest electron affinity are the best agents to release electrons to nitrogen. Elements of group IA and IIA readily transfer their valence electrons to nitrogen leading to the formation of nitride ion. Li_3N is rather easily formed by the combination of the elements little above the room temperature. Magnesium also forms Mg_3N_2 rather easily. In fact both Li and Mg can be used to remove nitrogen; other alkali nitrides K_3N, Na_3N, Rb_3N are difficult to prepare. They are obtained by striking an arc between Pt cathode and alkali metal anode in liquid nitrogen. Heating of a metal amide also gives nitride: $3Ba(NH_2)_2 \rightarrow Ba_3N_2 + 4NH_3$. The alkali metal nitrides are readily hydrolysed by water to form metal hydroxides. and ammonia:

$$Li_3N + 3H_2O \rightarrow 3LiOH + 3NH_3; Ca_3N_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2NH_3$$

These compounds have ionic crystal lattice and the radius of the nitride ion N^{3-} is 1.71A. Note how vastly the size of an atom increases on the formation of negative ions (atomic radius of nitrogen is only 0.7A) (cf. Chapter 4).

18.4.2. Covalent Nitrides : From the viewpoint of bonding most nitrides of groups IIIB, IVB, VB, VIB and VIIB and hydrogen are covalent. Some of these nitrides such as NH_3, NF_3, NCl_3, oxides of nitrogen etc. form simple volatile discrete covalent molecules whereas some others such as BN, AlN, InN form covalent but 'giant' molecules. Characteristic of giant molecules these latter nitrides have extremely high melting points and are extraordinarily hard. Boron nitride is made by heating $Na_2B_4O_7$ (or B_2O_3) and NH_4Cl. It has a graphite-like structure which changes to a diamond-like variety under pressure (Chapter 16).

18.4.3. Interstitial Nitrides : These nitrides are formed by transition metals. The small nitrogen atom occupies holes in the metallic lattice. Close packing of metal atoms creates octahedral holes and tetrahedral holes (Chapter 6). For an octahedral hole fitting the ratio of the small atom to that of the big metal atom should be in the range 0.41 to 0.73 (Chapter 6). Taking the atomic radius of nitrogen as 0.7A it follows that the metal atom radius should be within the range 1.2 to 1.7A. Stable nitrides are formed only by those transition metals (Ti, Zr, Nb etc.) whose radii are well within the above range. Radii of iron, manganese, cobalt, chromium etc. are rather borderline (~ 1.25A) and hence they do not form stable nitrides. As for tetrahedral hole fitting the nitrogen atom is much too big. Interstitial nitrides include nitrides of the MN type where M stands for an element of groups IIIA, IVA, VA eg: Sc, La, Ce, Pr; Ti, Zr; V, Nb, Ta. These nitrides are very hard and have high melting points. Other types of nitrides are Mo_2N, W_2N. Interstitial nitrides are commonly made by heating the powdered metal in nitrogen or in ammonia at ~ 1000°C. Some melting points are:

Nitride	TiN	ZrN	VN	NbN	TaN
M. P. (°C)	2947	2982	2300	2300	3087

18.5. COMPOUNDS OF THE GROUP VB ELEMENTS

18.5.1. Hydrides of Nitrogen : Nitrogen forms four hydrides: ammonia (NH_3), hydrazine (N_2H_4), hydroxylamine (NH_2OH) and hydrazoic acid (HN_3).

Ammonia. This is by far the most important hydride of this group. Laboratory synthesis involves reacting ammonium salts with a strong base:

$$NH_4Cl + NaOH \rightarrow NaCl + NH_3 + H_2O$$
$$2NH_4Cl + CaO \rightarrow CaCl_2 + 2NH_3 + H_2O$$

It may also be obtained by the hydrolysis of a metal nitride:

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$$

Industrially it is manufactured by the combination of elementary hydrogen and nitrogen:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + \text{heat}\ (\triangle H = -22\ \text{Kcal})$$

Le Chatelier's principle demands that yield will improve at high pressure and low temperature. The reaction being exothermic the higher the temperature the more unfavourable the equilibrium is, and again a decrease in volume of the product indicates that high pressure will favour the equilibrium. In practice 200—300 atmosphere pressure, a temperature of 450—550°C, and a catalyst made of iron and molybdenum (or iron with small amounts of potassium and aluminium oxide as promoters) are used. The unreacted gases are recycled. Both nitrogen and hydrogen must be very pure. The hydrogen is often obtained electrolytically and nitrogen from air by liquefaction and fractionation. Another important source is a mixture of producer gas ($CO + N_2$), water gas ($H_2 + CO + CO_2$) and steam properly worked up by passage over a catalyst followed by absorption of the undesired constituents. Passing air through a mass of red hot coke gives producer gas.

$$(4N_2 + O_2) + 2C \rightarrow 4N_2 + 2CO$$

Water gas is obtained by passing steam over red hot coke:

$$C + H_2O \rightarrow CO + H_2\ ;\ C + 2H_2O \rightarrow CO_2 + 2H_2$$

The mixture of producer gas and water gas in suitable proportion is led through a heated bed of a catalyst of ferric oxide and chromic oxide when CO is converted to CO_2 and H_2 is generated:

$$CO + H_2O \rightarrow CO_2 + H_2$$

The CO_2 in the exit gas is absorbed in water under pressure, and CO in ammoniacal cuprous formate solution also under pressure. CO_2 can also be scrubbed with a solution of ethanolamine which absorbs CO_2 forming ethanolamine carbonate.

Fixation of atmospheric nitrogen is also done by the cyanamide process. The process is based on the reaction of nitrogen gas with calcium carbide in an electric furnace at ~ 1000°C. Calcium carbide is finely ground and powdered CaF_2 is added to serve as a catalyst. The mixture is then heated in nitrogen at ~ 1000°C when calcium cyanamide is formed:

$$CaC_2 + N_2 \rightarrow CaNCN + C$$

The cyanamide is then acted upon by steam to form NH_3 and $CaCO_3$:

$$CaNCN + 3H_2O \rightarrow 2NH_3 + CaCO_3$$

The carbonate can be decomposed at ~ 1000°C to $CaO + CO_2$, the CaO made to combine with carbon at ~ 3000°C to give CaC_2 which is then recycled.

Ammonia is used extensively in the syntheses of nitrogenous fertilisers $(NH_4)_2SO_4$ and $(NH_4)_3PO_4$. It can be oxidised on the surface of a hot platinum gauze catalyst to form NO which can then be converted in the presence of oxygen to NO_2 and finally to HNO_3. The nitric acid, in turn, is extensively used in pharmaceuticals, dyes and explosives.

Ammonia molecule is pyramidal with the lone pair occupying the fourth sp^3 hybrid orbital. The repulsion exerted by the lone pair on the bond pairs forces a small closing up of the bond angle from 109° to 107°. It is highly associated due to hydrogen bonding. It is an ionising solvent. It is a strong proton acceptor so that acetic acid, a weak acid in water, turns out to be a strong acid in liquid ammonia. It is a strong donor.

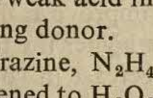
Hydrazine: Hydrazine, N_2H_4, may be viewed as an oxidation product of NH_3, and may be likened to H_2O_2 which may be viewed as an oxidation product of H_2O. It is obtained by oxidising aqueous ammonia by hypochlorite under boiling in the presence of glue or gelatin:

$$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH; \; NH_2Cl + 2NH_3 \rightarrow NH_2.NH_2 + NH_4Cl$$

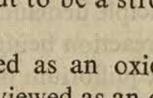
Presence of glue or gelatin serves to minimise the oxidation of hydrazine to nitrogen by chloramine:

$$N_2H_4 + 2NH_2Cl \rightarrow N_2 + 2NH_4Cl$$

After the reaction is over the solution is cooled in ice and treated with sulphuric acid when hydrazine sulphate $N_2H_4.H_2SO_4$ crystallises. Treating the sulphate with alkali produces hydrazine hydrate $N_2H_4.H_2O$ and free hydrazine can be recovered by distillation under reduced pressure. It melts at 2°C and boils at 114°C. Hydrazine has the structures: (18—Ia; 18—Ib).



(18-Ia)



(18-Ib)

Assuming each nitrogen to be sp^3 hybridised it follows there are two lone pairs of electrons in N_2H_4. It behaves as a diacidic base:

$$N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^- ; \quad K_B^I \sim 10^{-6}$$

$$N_2H_5^+ + H_2O \rightleftharpoons N_2H_6^{2+} + OH^- ; \quad K_B^{II} \sim 10^{-15}$$

Thus two series of hydrazinium salts are possible, the monoacidic ones being stable in aqueous solution.

Like H_2O_2, hydrazine shows reducing properties, and to some extent oxidising properties. Hydrazine hydrate and its salts convert iodates to iodides, halogens to halides, iron (III) to iron (II) etc:

$$N_2H_4 + 2Cl_2 \rightarrow N_2 + 4HCl\ ;\quad N_2H_4 + 4FeCl_3 \rightarrow N_2 + 4FeCl_2 + 4HCl$$

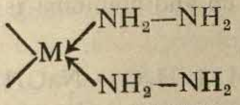
In presence of Zn and HCl, N_2H_4 is reduced to NH_3:

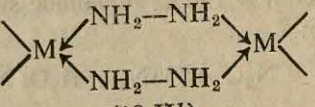
$$N_2H_4 + Zn + 2HCl \rightarrow 2NH_3 + ZnCl_2$$

Hydrazine is a good ionising solvent (dielectric constant 53). It often reacts explosively with certain metals to give ammonia, hydrogen and nitrogen. It dissolves alkali metals to give blue solution (cf: liquid ammonia) which slowly give metal hydrazide and hydrogen:

$$N_2H_4 + Na \rightarrow NaN_2H_3 + \tfrac{1}{2}H_2$$

Hydrazine can function either as a monodentate ligand (18-II*a*) or as a bridging ligand using both the lone pairs (18-II*b*). It should be noted, however, it cannot serve as a bidentate ligand because of the strain resulting from a three-membered ring at the metal. The two lone pairs do not converge on the metals (cf: 18-I*a*).


(18-II*a*)


(18-II*b*)

Hydroxylamine: This may be thought of as derived from ammonia by the replacement of one H by an OH. Hydroxylamine may be obtained by the reduction of nitrites by SO_2 or by the electrolytic reduction of HNO_3 at a lead cathode. A concentrated solution of $NaNO_2$ is mixed with a solution of Na_2CO_3, and SO_2 led in till the solution is acidic. The solution is now acidified with dilute H_2SO_4 and heated to 90°C in order to hydrolyse the sodium salt of hydroxylamine disulphonate (formed in the initial step) to hydroxylamine sulphate:

$$Na_2CO_3 + 2SO_2 + H_2O \rightarrow 2NaHSO_3 + CO_2$$
$$NaHSO_3 + NaNO_2 \rightarrow Na_2SO_3 + HNO_2$$
$$HO.NO + 2Na_2SO_3 \rightarrow HO.N(SO_3Na)_2 + Na_2O$$
$$HO.N(SO_3Na)_2 + 2H_2O \rightarrow HO.NH_2.H_2SO_4 + Na_2SO_4$$

The cathodic reduction of HNO_3 at a lead cathode may be represented as:

$$HONO_2 + 6H^+ + 6e \rightarrow HO.NH_2 + 2H_2O$$

Anhydrous hydroxylamine NH_2OH can be obtained by distilling the sulphate or the chloride in presence of alkali under reduced pressure. Free hydroxylamine is a white solid (M. P. 33°C) which readily decomposes.

Replacement of one H in NH_3 by an $-OH$ (in NH_2OH) connects nitrogen to a more electronegative oxygen, and the result is a lowering of the base strength from NH_3 to NH_2OH ($K_B \sim 6.0 \times 10^{-6}$; K_B of $NH_3 \sim 10^{-5}$). Hydroxylamine can serve both as a reducing agent and as an oxidising agent. It reduces ferric to ferrous, cupric oxide to cuprous, gold (III) chloride to gold, the hydroxylamine being oxidised to N_2O:

$$2NH_2OH + 4FeCl_3 \rightarrow N_2O + 4FeCl_2 + 4HCl + H_2O$$
$$2NH_2OH + 4CuO \rightarrow N_2O + 2Cu_2O + 3H_2O$$

In alkaline solution, however, it oxidises ferrous hydroxide to ferric hydroxide and is itself reduced to ammonia:

$$2Fe(OH)_2 + NH_2OH + H_2O \rightarrow 2Fe(OH)_3 + NH_3$$

By virtue of the lone pair of electrons on the nitrogen it can serve as a ligand, coordinating through nitrogen, e.g. in $[Zn(NH_2OH)_2Cl_2]$.

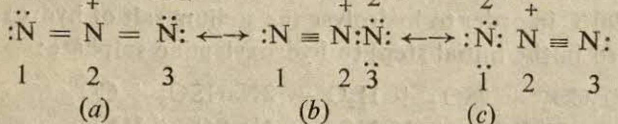
Hydrazoic acid: It is obtained by the interaction of sodamide and N_2O. Sodamide, $NaNH_2$, is first prepared by passing dry ammonia over sodium at ~ 200°C:

$$2Na + 2NH_3 \rightarrow 2NaNH_2 + H_2$$

The ammonia is then chased off by a current of dry N_2O and sodamide made to react with N_2O at ~ 190°C. Sodamide swells up and ammonia is evolved in a secondary step:

$$NaNH_2 + N_2O \rightarrow NaN_3 + H_2O; \; NaNH_2 + H_2O \rightarrow NaOH + NH_3$$

After the evolution of ammonia has ceased, the mass is cooled and distilled with dilute sulphuric acid to get aqueous HN_3. The aqueous solution on further distillation in the presence of anhydrous $CaCl_2$ provides anhydrous HN_3. The anhydrous material is dangerously explosive. It is a liquid boiling at 37°C. In aqueous solution it is a weak acid ($K_A \sim 10^{-5}$). The azide ion is a pseudohalide and forms salts with several metal ions. The azide ion also forms complexes like the halides and its position is close to chloride in the spectrochemical series. The structure of N_3^- ion is a resonance hybrid of the following individual forms (18-III; *a, b, c*):



$$\overset{\overline{}}{:\ddot{N}} = \overset{+}{N} = \overset{-\overline{}}{\ddot{N}}: \longleftrightarrow :N \equiv \overset{+}{N}:\overset{2-}{\ddot{N}}: \longleftrightarrow :\overset{2-}{\ddot{N}}: \overset{+}{N} \equiv N:$$

(18-III)

The three nitrogens are linear but when the ion coordinates as a monodentate ligand through one of the end nitrogens the metal—nitrogen bond is at an angle to the linear N_3^- unit. The end nitrogens of structure (18-III; *a*) are sp^2 hybridised. One sp^2 houses a lone pair, another sp^2 makes a coordinate link to the metal ion.

$$N\,\underset{2s}{\underline{\uparrow\downarrow}}\;\underset{2p}{\underline{\uparrow}}\;\underset{2p}{\underline{\uparrow}}\;\underset{2p}{\underline{\uparrow}} + \text{one electron} \xrightarrow{\text{hybridises}} \underset{2(sp^2)}{\underline{\uparrow\downarrow}}\;\underset{2(sp^2)}{\underline{\uparrow\downarrow}}\;\underset{2(sp^2)}{\underline{\uparrow}}\;\underset{2p}{\underline{\uparrow}}$$

The third sp^2 with one unpaired spin makes a bond with the middle nitrogen. The third p orbital makes a π-overlap with the middle N completing the double bond. In keeping with sp^2 hybridisation the $H—N_3$ bond angle in the free acid is 110° and the C—N_3 bond angle in methyl azide $H_3C—N_3$ is ~ 130°. Note that the nitrogen marked 3 in structure (18-III; *b*) or the nitrogen marked 1 in structure (18-III; *c*) have four pairs of electrons (sp^3 hybridisation) so that metal —N_3 bond angle should be around ~ 109°. Also note that the triple bonded nitrogen marked 1 in (18-III; *b*) and marked 3 in (18-III; *c*) should give a linear metal azide link.

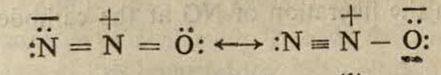
18.5.2. Oxides of Nitrogen : Recall that nitrogen forms the following oxides:

Oxidation Number	+1	+2	+3	+4	+5
Formula	N_2O	NO	N_2O_3	NO_2 or N_2O_4	N_2O_5
Boiling Point (°C)	−88	−152	3.5 (decomp)	21 (decomp)	47 (decomp)

Nitrous Oxide: It is obtained by the thermal decomposition of ammonium nitrate at ~ 250°C:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

The accompanying impurities such as NO is absorbed in ferrous sulphate solution (giving brown $FeSO_4.NO$). It does not react with halogens, alkalies or even with ozone at room temperature. However at higher temperature it becomes active due to its own decomposition into nitrogen and oxygen. It is a neutral oxide and does not form with water hyponitrous acid ($H_2N_2O_2$) nor gives hyponitrites with alkalies. Hence it cannot be regarded as the anhydride of hyponitrous acid. It is a linear molecule with the following resonating structures (18-IV; *a*, *b*):



$$\overset{-}{:\ddot{N}} = \overset{+}{N} = \ddot{O}: \longleftrightarrow :N \equiv \overset{+}{N} - \overset{-}{\underset{\cdot\cdot}{\ddot{O}}}:$$

(*a*) (18-IV) (*b*)

In structure (18-IV, *a*) the central nitrogen (with 4 electrons) uses *sp* hybridisation with one unpaired electron on each of the two *sp* and the remaining two *p* orbitals. The two linear *sp* hybrids overlap with suitable *p* orbital (p_x, if *x* axis is taken as the bond axis) of oxygen on one side and of nitrogen on the other side. The remaining two *p* orbitals overlap with suitable *p* orbitals of oxygen (say p_y) and of nitrogen (say p_z) to form the double bonds (π-bonds). In structure (18-IV, *b*) the central nitrogen makes two π-bonds to the other nitrogen and one sigma bond (*sp* hybrid) each to nitrogen and oxygen. *sp* hybridisation of the terminal oxygen and nitrogen may also be conceived for overlap with the orbitals of the central nitrogen. The gas is used as an anaesthetic.

$$\frac{\uparrow}{2(sp)} \quad \frac{\uparrow}{2(sp)} \quad \frac{\uparrow}{2p} \quad \frac{\uparrow}{2p}$$

Nitric Oxide: This is made on commercial scale by oxidising ammonia with air over a platinum catalyst at ~ 500°C:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

This is obtained also by the reduction of nitrites or nitrates:

$$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$$
$$8HNO_3 + 3Cu \rightarrow 2NO + 3Cu(NO_3)_2 + 4H_2O$$

It is readily oxidised to $NO_2(N_2O_4)$ in air or to nitrosyl halides NOF, NOCl, NOBr by the respective halogens. Strong oxidants convert it to N_2O_5 or HNO_3 (in presence of water). SO_2 reduces NO to N_2O and chromous ion in acid solution reduces NO to NH_2OH.

Its rich chemistry arises out of its odd electron behaviour. The molecule has $5 + 6 = 11$ electrons in its outer quantum shell. Reactions of NO can be grouped under the following heads:

A. The unpaired electron in the π^* antibonding orbital (Chapter 5) is easily lost to give the nitrosyl cation $[NO]^+$. A variety of compounds $NOHSO_4$, $NOBF_4$, $NOClO_4$ are known with the nitrosyl cation. These compounds are synthesised by passing N_2O_3 through the respective anhydrous acids:

$$N_2O_3 + 2H_2SO_4 \rightarrow 2NOHSO_4 + H_2O$$

$$N_2O_3 + 2HClO_4 \rightarrow 2NOClO_4 + H_2O$$

$$N_2O_3 + 2HBF_4 \rightarrow 2NOBF_4 + H_2O$$

Some salts containing NO^+ have also been prepared by reacting nitrosyl chloride with suitable anhydrous halides: $NOCl + SbCl_5 \rightarrow NO[SbCl_6]$. Salts of nitrosyl cation are moisture sensitive and are to be handled in dry atmosphere. Nitrosyl bisulphate or nitrosyl sulphuric acid, $NOHSO_4$, is an intermediate in the synthesis of H_2SO_4 by the lead chamber process. This is known as chamber crystal. That all these compounds are ionic and contain NO^+ is shown by their uni-univalent conductance in suitable non-aqueous solvents. Electrolysis of $NOHSO_4$ in anhydrous H_2SO_4 results in the liberation of NO at the cathode being detected by brown vapour in air:

$$NOHSO_4 \rightarrow NO^+ + HSO_4^-$$

$$\text{at the cathode:}\quad NO^+ + e \rightarrow NO;\ 2NO + O_2 \rightarrow 2NO_2$$

Crystal structures of $NOBF_4$ and NH_4BF_4 are comparable.

B. The molecule can participate in covalent bond formation without losing the odd electron. Nitrosyl halides are typical examples:

$$2NO + F_2 \xrightarrow{\text{Copper tube}} 2FNO;\ 2NO + Br_2 \xrightarrow{15°C} 2BrNO$$

$$N_2O_4 + KCl \longrightarrow ClNO + KNO_3$$

These compounds are largely covalent as shown be their volatility and non-conducting behaviour. Structural studies show that the halogen atom is connected to nitrogen and the molecule is bent. The nitrogen-chlorine bond length in ClNO is longer than would follow from the single bond covalent radii (N, 0.70A + Cl, 0.99A = 1.69A; experimental, 1.95A). This is an indication that some polar character is present. The Cl—N—O angle is 116°. The nitrogen atom is sp^2 hybridised. One sp^2 houses a lone pair while another sp^2 with one electron overlaps with a chlorine p electron. The third sp^2 electron makes a sigma overlap with oxygen. The remaining electron in the p orbital of nitrogen makes a pi overlap with an oxygen p electron. The molecule has an overall V shape (see Part I' page 129).

C. NO^+ ion is isoelectronic with CO and its M.O. diagram has the same electron distribution as CO. NO^+ ion is electron deficient and can participate in low oxidation state stabilisation. Whereas CO is a two-electron donor, NO is a three-electron donor. Conceptually we may assume that the odd electron is first transferred to an orbital of the metal ion, thus reducing its valence by one unit and then NO^+ coordinates just as CO does.

$$M + NO \rightarrow M^- + NO^+ \rightarrow M^- \leftarrow NO^+$$

Common examples of nitrosyl complexes are sodium nitroprusside $Na_2[Fe(CN)_5NO]$, $[Mn(NO)_3CO]$, $[Co(CO)_3NO]$ etc. For details see Chapter 23.

The MO picture of NO has been described in Chapter 5. In valence bond model this may be viewed as a resonance hybrid (18-V).

$$\underset{(a)}{:\dot{N} = \ddot{O}:} \longleftrightarrow \underset{(b)}{:\overset{-}{\ddot{N}} = \overset{+}{\dot{O}}:}$$

(18.V)

We may assume that nitrogen uses *sp* hybridisation—one *sp* in structure (18-V, *a*) carrying the lone pair and another *sp* with one electron overlapping with one oxygen orbital (say p_x). The unpaired electron in one *p* orbital of nitrogen (say p_y) then overlaps with a suitable *p* orbital (say p_y) of oxygen. Another *p* orbital of the nitrogen has the odd *electron*. In (18-V, *b*) the situation is reversed.

Nitrogen Sesquioxide or *Dinitrogen Trioxide:* N_2O_3 (M.P.−102°C) is known only in the solid state at low temperature. It is obtained by mixing NO and O_2 in 1:1 proportion or NO and NO_2 in 1:1 proportion. It may be considered as the anhydride of nitrous acid since it dissolves in water to give the acid HNO_2 or nitrite salts in alkali solution. The acid and its salts are reducing agents towards $KMnO_4$ or the halogens but oxidants to N_2O, NO, HI, iron (II) etc. (see HNO_2). It is believed that the structure of N_2O_3 involves a link between O_2N and NO via a π-bond. Both NO_2 and NO have an odd electron which make the π-bond.

Nitrogen Dioxide or *Dinitrogen Tetroxide:* The brown nitrous fumes that we encounter in the laboratory contain the monomer form NO_2. This is obtained by heating a heavy metal nitrate:

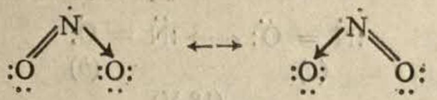
$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$$

The gas can be condensed first to a brown liquid which on further cooling turns colourless due to dimerisation: $2NO_2$ (brown, paramagnetic) $\rightleftharpoons N_2O_4$ (colourless, diamagnetic). On dimerisation the odd electron character is lost. NO_2 is absorbed in alkalies to give a mixture of nitrite and nitrate: $2KOH + 2NO_2 \rightarrow KNO_2 + KNO_3 + H_2O$. Metals react with liquid N_2O_4 to form metal nitrates and NO: $K + N_2O_4 \rightarrow KNO_3 + NO$, N_2O_4 dissolves in solvents of high dielectric constant such as $HClO_4$, HNO_3 and H_2SO_4 to dissociate into nitrate anion and nitrosyl cation: $N_2O_4 \rightleftharpoons NO^+ + NO_3^-$.

The bonding in NO_2 can be described in the following terms. We assume sp^2 hybridisation in nitrogen with two electrons in one sp^2 hybrid, the other three electrons being distributed one each in the two other sp^2 hybrids and the remaining p_z orbital. The paired electrons are donated to one oxygen forming a coordinate

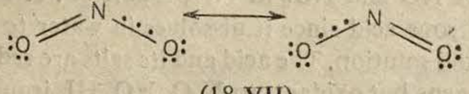
$$\mathrm{N}\,\underset{2s}{\underline{\uparrow\downarrow}}\;\underset{2p}{\underline{\uparrow}}\;\underset{2p}{\underline{\uparrow}}\;\underset{2p}{\underline{\uparrow}}\quad \text{hybridises to}\quad \underset{2(sp^2)}{\underline{\uparrow\downarrow}}\;\underset{2(sp^2)}{\underline{\uparrow}}\;\underset{2(sp^2)}{\underline{\uparrow}}\;\underset{2p_z}{\underline{\uparrow}}$$

bond. The second sp^2 orbital overlaps with one unpaired electron of an orbital of the second oxygen to make a sigma bond. The third sp^2 orbital houses one unpaired spin and remains located on the nitrogen. The p_z orbital of nitrogen now overlaps with one unpaired electron in a p_z orbital of oxygen. This overlap gives a π-bond, thus completing the double bond. Thus NO_2 can be described by the following two resonance forms (18-VI).



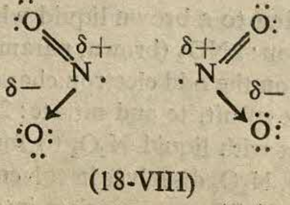
(18-VI)

The N—O distance is 1.19A. Single bond covalent radius would give $0.70 + 0.66 = 1.36$A. This indicates that N—O bond has significant double bond character, and hence the above resonating structures. However, the O—N—O bond angle (132°) is larger than the sp^2 bond angle of 120°. The reader should also note that the resonating structures (18-VI) are also often expressed as three-electron bond structures (18-VII):



(18-VII)

The dimeric N_2O_4 is planar with long N—N bond which is much longer than the N—N bond in hydrazine. O—N—O bond angle is ~ 134°. Invoking sp^2 hybridisation of both the nitrogens and allowing overlap of the sp^2 hybrids carrying the odd electron on each nitrogen we can write the following structure for N_2O_4 (18-VIII): Such structure admits of some δ^+ charge on each nitrogen so that repulsion between adjacent δ^+ charges will make the N—N bond longer than a single bond.



(18-VIII)

Dinitrogen Pentoxide: This is made by the dehydration of HNO_3 by P_4O_{10}

(commonly called phosphorus pentoxide) and recovered by distilling in a current of ozone:

$$4HNO_3 + P_4O_{10} \rightarrow 4HPO_3 + 2N_2O_5$$

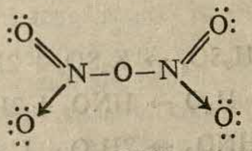
It is also obtained by the action of Cl_2 on $AgNO_3$:

$$4AgNO_3 + 2Cl_2 \rightarrow 4AgCl + 2N_2O_5 + O_2$$

In anhydrous H_2SO_4 or HNO_3 it dissociates into NO_2^+ and NO_3^-:

$$N_2O_5 \rightleftharpoons NO_2^+ + NO_3^-$$

It is to be regarded as the anhydride of HNO_3. The oxide is unstable and often explodes. In the gaseous state it exists in a molecular form with the following structure (18-IX):



(18-IX)

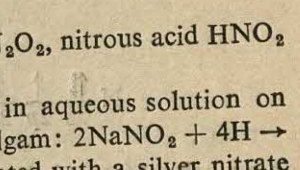
The N—O—N link is almost linear. The structure of N_2O_5 has a connection with that of N_2O_4 (18-VIII). The single electron on each nitrogen of O_2N unit of (18-VIII) overlaps with an unpaired electron of *sp* hybridised oxygen. The N—O—N link cannot be linear unless *sp* hybridisation of oxygen is assumed:

$$\mathrm{O}\ \underset{2s}{\underline{\uparrow\downarrow}}\ \underset{2p}{\underline{\uparrow\downarrow}}\ \underset{2p}{\underline{\uparrow}}\ \underset{2p}{\underline{\uparrow}}\ \text{hybridises to}\ \underset{2(sp)}{\underline{\uparrow}}\ \underset{2(sp)}{\underline{\uparrow}}\ \underset{2p}{\underline{\uparrow\downarrow}}\ \underset{2p}{\underline{\uparrow\downarrow}}$$

The gaseous N_2O_5 changes to a solid one at low temperature, when the compound is best written in an ionic form $NO_2^+NO_3^-$. The nitronium ion is linear $[O = N = O]^+$ like CO_2 and the nitrate ion is symmetrical planar (sp^2 hybridisation of nitrogen).

18.5.3. Oxyacids of Nitrogen: Hyponitrous acid $H_2N_2O_2$, nitrous acid HNO_2 and nitric acid HNO_3, and their salts are known.

Hyponitrous Acid: Sodium hyponitrite is formed in aqueous solution on treating a solution of sodium nitrite with sodium amalgam: $2NaNO_2 + 4H \rightarrow Na_2N_2O_2 + 2H_2O$. The solution is neutralised and treated with a silver nitrate solution to precipitate $Ag_2N_2O_2$. The silver salt, on being treated with HCl, precipitates AgCl. The free acid can be extracted into ether and crystallised. The acid is very weak ($K_A \sim 10^{-7}$). The structure of the hyponitrite ion is shown in (18-X). Each oxygen may be assumed to have acquired one electron during anion formation. Each nitrogen is sp^2 hybridised. In one of the three sp^2 orbitals of nitrogen resides the lone pair. The two other sp^2 orbitals with one unpaired spin overlap with an orbital of oxygen carrying the extra electron, and with a similar orbital of the other nitrogen. Finally the remaining *p*-orbitals of the two nitrogen



(18-X)

with one unpaired electron on each overlap to make the second bond (π type). Hyponitrous acid reduces permanganate in acid medium:

$$5H_2N_2O_2 + 8KMnO_4 + 12H_2SO_4 \rightarrow 10HNO_3 + 4K_2SO_4 + 8MnSO_4 + 12H_2O$$

Nitrous Acid: The free acid is known only in solution. It is formed when N_2O_3 is absorbed in water at 0°C: $N_2O_3 + H_2O \rightarrow 2HNO_2$. Metal nitrites are obtained by absorption of N_2O_3 in alkalies: $2NaOH + N_2O_3 \rightarrow 2NaNO_2 + H_2O$. Alkali metal nitrites are also conveniently made by reducing metal nitrates with metals like lead, iron or even carbon: $NaNO_3 + Pb \rightarrow NaNO_2 + PbO$. The fused mass may be extracted with water and the alkali nitrite evaporated to crystallisation. Nitrous acid is a weak acid ($K_A \sim 10^{-6}$). Nitrites and the nitrous acid are reducing agents towards $KMnO_4$ and the halogens but oxidants to N_2O, NO, HI, iron (II) etc:

$$2KMnO_4 + 5NaNO_2 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5NaNO_3 + 3H_2O$$

$$HNO_2 + Br_2 + H_2O \rightarrow HNO_3 + 2HBr$$

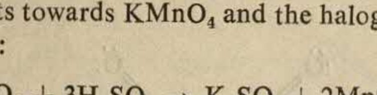
$$2HI + 2HNO_2 \rightarrow 2H_2O + I_2 + 2NO$$

$$FeCl_2 + HNO_2 + HCl \rightarrow FeCl_3 + NO + H_2O$$

$$2SnCl_2 + 2HNO_2 + 4HCl \rightarrow 2SnCl_4 + N_2O + 3H_2O$$

$$SO_2 + 2HNO_2 \rightarrow H_2SO_4 + NO$$

The nitrite ion NO_2^- possesses a planar triangular structure with sp^2 hybridisation of nitrogen. The resonating structures (18-XI) can be written. One of the sp^2 hybrids houses the lone pair. The two other sp^2 hybrids overlap with *p* orbitals of the two oxygen atoms forming two covalent bonds. The fifth electron of nitrogen



(18-XI)

$$N \, \frac{\uparrow\downarrow}{2s} \, \frac{\uparrow}{2p} \, \frac{\uparrow}{2p} \, \frac{\uparrow}{2p} \text{ hybridises to } \frac{\uparrow\downarrow}{2(sp^2)} \, \frac{\uparrow}{2(sp^2)} \, \frac{\uparrow}{2(sp^2)} \, \frac{\uparrow}{2p}$$

on a *p* orbital (say p_z) then makes a π-overlap with another unpaired electron in a suitable *p*-orbital (say p_z) of oxygen to complete the double bond. The octet of the other oxygen is completed by gaining the extra electron resulting from the negative charge on the NO_2^- ion.

An interesting feature of the nitrite ion is its ability to coordinate to a metal ion via nitrogen (*nitro complexes*) or via oxygen (*nitrito complexes*). The ion therefore shows *ambidentate* behaviour and can give rise to *linkage isomers.* The nitroform is a stronger ligand than the nitrito form (Part I, p. 214).

Nitric Acid: On a commercial scale nitric acid is obtained by three processes: A. Nitre Process B. Oxidation of atmospheric nitrogen and C. Oxidation of ammonia.

A. Nitre Process: This is an old process where sodium nitrate (Chile saltpetre) is heated with equal weight of concentrated sulphuric acid in iron retorts:

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3.$$

The resulting vapour of nitric acid is condensed in water-cooled silica pipes and the concentrated HNO_3 is collected in stoneware vessels. The uncondensed vapour is dissolved in water in absorption towers packed with stoneware balls in a counter current principle. The dilute acid is then mixed with the stream of concentrated acid and recirculated till the desired concentration is obtained.

B. *Oxidation of Atmospheric Nitrogen:* Atmospheric nitrogen and oxygen are forced to combine to form NO : $N_2 + O_2 \rightleftharpoons 2NO$. The above reaction being endothermic and indicating no change in volume Le Chatelier's principle says that the reaction will be favoured by temperature rise but will remain unaffected by pressure. The best condition is a temperature of $\sim$ 3000°C (set by an electric arc) followed by rapid cooling of the gas. Slow cooling leads to a backward rush of the reaction. The gas is then led to oxidation chambers where NO combines with excess oxygen to give the dioxide NO_2. The gas is then forced into absorption towers filled with quartz pieces where NO_2 is made to react with further air and water to form nitric acid.:

$$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$$

The method is nowadays obsolete since ammonia oxidation method turned out to be cheaper.

C. *Ammonia Oxidation Method:* Ammonia undergoes different types of oxidation reactions under varied conditions. In air ammonia reacts but little to form nitrogen. In pure oxygen it burns with the formation of nitrogen and water:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

Over a hot platinum gauze catalyst a mixture of NH_3 and air in the ratio of 1 : 7 is oxidised mostly to NO:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

The liberated heat keeps the catalyst hot. The NO is cooled and is mixed with oxygen to give the dioxide. The product is then passed into warm water under pressure to give nitric acid:

$$4NO_2 + 2H_2O + O_2 \rightarrow 4HNO_3$$

Commercially available concentrated HNO_3 is about 98%. Fuming HNO_3 contains additionally dissolved NO_2 and has a yellow colour. Aqua regia is 3 parts concentrated HCl plus 1 part concentrated HNO_3, and this contains free chlorine and ClNO. That aqua regia is a more powerful oxidant and dissolving agent than HNO_3 must be due, to a large extent, to the joint action of chlorine and ClNO as oxidants, and of chloride ion as complexing ligand.

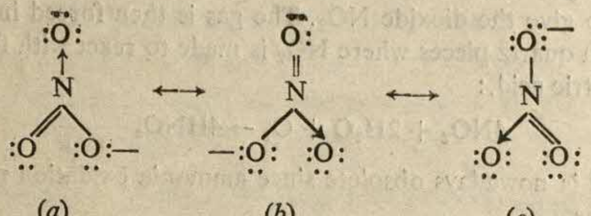
Chemical activities of nitric acid may be summarised under the following three heads: behaviour as an acid, as an oxidant and as a nitrating agent. In aqueous solution it is a very strong acid. Some of its oxidising activities are shown by the following reactions:

$$Cu + 4HNO_3\,(\text{concentrated}) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$
$$Cu + 8HNO_3\,(\text{dilute}) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$
$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

Concentrated HNO_3 in the presence of concentrated H_2SO_4 attacks aromatic hydrocarbons and their derivatives giving nitro compounds; sulphuric acid serves to absorb the water:

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$$
$$C_6H_5OH + 3HNO_3 \rightarrow C_6H_2(NO_2)_3OH + 3H_2O$$

The nitrate ion is planar and symmetrical, the O—N—O angle being 120°. The structure may be represented by the following resonating forms (18-XII; *a*, *b*, *c*):



(*a*) (*b*) (*c*)

(18-XII)

Evidently sp^2 hybridisation of nitrogen is involved. One sp^2 orbital with two electrons forms the coordinate link. The other two sp^2 orbitals with single electron on each forms two single covalent bonds to the other two oxygen atoms. The remaining nitrogen electron in a *p* orbital makes a π-overlap with a suitable *p* orbital of oxygen. One of the three oxygens (with '—' sign) acquires an electron due to a negative charge of the NO_3^- ion. The N—O bond length (1.22A) being shorter than single bond length $(0.70 + 0.66 = 1.36A)$ suggests resonance. The nitrate ion is a poor ligand coordinating through oxygen forming nitrato complexes.

18.5.4. Halides of Nitrogen: Nitrogen forms two trihalides NF_3 and NCl_3. Besides, several mixed halides have also been reported: NF_2Cl, $NFCl_2$ as also N_2F_2 and N_2F_4. We discuss only the simpler varieties.

On electrolysis of fused NH_4HF_2 in a copper vessel very complicated reactions take place with evolution of gases such as HF, N_2, N_2O, O_2, O_3, NH_2F, NHF_2 and NF_3. The mixture is passed over KF to arrest HF, over MnO_2 to remove O_3, and is then frozen and distilled. The liberated gas is washed with alkali to absorb NHF_2 and NH_2F. Finally NF_3 is obtained as a colourless gas (B. P. −119°C). It is a very stable compound and remains unaffected by water. It has a pyramidal structure (sp^3 hybridisation) with one lone pair of electrons completing the fourth sp^3 orbital of nitrogen. The donor property of NH_3 is very poor because of the highly electronegative fluorines. It acts as a donor towards a strong Lewis acceptor BF_3 only to form the adduct $F_3N \rightarrow BF_3$.

Nitrogen trichloride is obtained as a pale yellow oil (B. P. ~ 70°C) in the chlorination of slightly acidic NH_4Cl solution:

$$NH_4Cl + 3Cl_2 \rightarrow NCl_3 + 4HCl$$

This is a highly explosive liquid. It is completely hydrolysed by water into ammonia and hypochlorous acid:

$$NCl_3 + 3H_2O \rightarrow NH_3 + 3HClO$$

We have already mentioned that the hydrolysis of NCl_3, as opposed to NF_3, is facilitated by the availability of *d*-orbitals in chlorine. It is a general experience that wherever a chlorine and a fluorine compound of the same type exist, the fluorine compound is more stable: UF_6 is stabler than UCl_6; BF_4^- is stabler than BCl_4^-, and NF_3 is stabler than NCl_3 etc.

Note in particular that no nitrogen halides are known with an oxidation number + 5. This is because nitrogen has no *d*-orbital available for suitable hybridisation of the sp^3d or sp^3d^2 type.

Chloramine: It is produced in aqueous solution by the interaction of hypochlorite and ammonia:

$$NH_3 + KClO \rightarrow NH_2Cl + KOH$$

On distilling the reaction mixture in vacuo chloramine is obtained in the distillate as a yellow oil. It is hydrolysed by water to ammonia and hypochlorous acid. It is a powerful oxidising agent.

Bromine reacts with ammonia below pH 6 to give NBr_3. This can beextracted into chloroform but decomposes rather rapidly. Iodine and concentrated ammonia give the black explosive compound $NI_3.NH_3$.

18.5.5. Hydrides of Phosphorus: Phosphorus forms two hydrides, phosphine PH_3 and diphosphine P_2H_4, being formally analogous to NH_3 and N_2H_4. Elementary phosphorus reacts with H_2 at ~ 300°C to form PH_3. The hydrolysis of metal phosphides is a convenient route to PH_3:

$$Ca_3P_2 + 6H_2O \rightarrow 2PH_3 + 3Ca(OH)_2$$

White phosphorus also reacts with hot water to produce phosphine and hypophosphorous acid:

$$4P + 6H_2O \rightarrow PH_3 + 3H_3PO_2$$

Aqueous NaOH facilitates the reaction. It is a colourless gas with an odour of rotten fish. Unlike NH_3, PH_3 is not a base. Its solution in water is neither acidic nor basic. It is a far weaker electron donor than ammonia and its complexes are little known. Phosphonium halides can be prepared by the reaction of phosphine with hydrogen halides but these compounds appear to be primarily covalent and are dissociated in the vapour phase. In water the phosphonium halides are completely hydrolysed to phosphine, halide ion and H_3O^+ ion.

$$PH_4I + H_2O \rightarrow PH_3 + I^- + H_3O^+$$

Phosphine is a stronger reducing agent than ammonia, reducing many heavy metal ions to the free metals or to metal phosphides. It is highly poisonous.

$$3AgNO_3 + PH_3 \rightarrow Ag_3P + 3HNO_3$$
$$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2 + 3H_2SO_4$$
$$Ag_3P, 3AgNO_3 + 3H_2O \rightarrow 6Ag + 3HNO_3 + H_3PO_3$$

Diphosphine is produced in small quantity along with phosphine and can be separated from PH_3 by condensing as a yellow liquid (B.P. 52°C). On heating it decomposes:

$$3P_2H_4 \rightarrow 2P + 4PH_3$$

It is a strong reducing agent and has some properties analogous to those of hydrazine.

18.5.6. Oxides of Phosphorus: Phosphorus forms two oxides in the oxidation states + 3 (P_4O_6) and + 4 (P_4O_{10}). The lower oxide is made by passing a mixture of oxygen and nitrogen (as diluent) in the 3 : 1 ratio by volume over white phosphorus around 50°C. Phosphorus burns to produce a mixture of P_4O_6 alongwith a small quantity of the pentoxide. The solid P_4O_{10} is retained with the help of a plug of glass wool, and the P_4O_6 is condensed. P_4O_6 is a snow white waxy solid (M.P. ~ 24°C). It slowly dissolves in water to form phosphorous acid:

$$P_4O_6 + 3H_2O \rightarrow 2H_3PO_3$$

Burning phosphorus in excess of air gives P_4O_{10}. It is purified by sublimation at 360°C in a current of dry oxygen. It has an extremely strong affinity for water and is used as a celebrated drying agent:

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

It can extract water even from sulphuric acid and nitric acid giving SO_3 and N_2O_5 respectively.

The structures of both P_4O_6 and P_4O_{10} are based on the tetrahedral skeleton of elementary phosphorus. Note each tetrahedron possesses six edges and along each edge is one oxygen giving P_4O_6 structure. Each phosphorus is tricovalent and the angles P—O—P are ~ 127° and O—P—O angle ~ 99°. Recall that for elementary P_4 molecule we had to invoke strained $p-p$ covalent bonds since P—P—P angles are ~ 60°. In P_4O_6 the bond angles suggest that each oxygen is sp^2 hybridised and each phosphorus is roughly tetrahedral (sp^3 ideal angle 109°). Three of the sp^3 hybrid orbitals of phosphorus overlap with sp^2 hybrid orbitals of oxygen, and a lone pair is left unused on the fourth sp^3 orbital of phosphorus. In P_4O_{10} we have another four oxygens over P_4O_6. Each phosphorus of P_4O_6 is

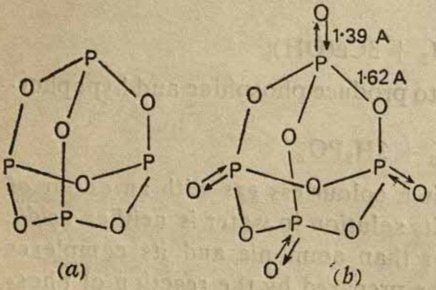
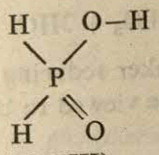
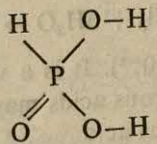


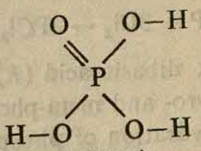
Fig. 18.3. Structures of (a) P_4O_6 and (b) P_4O_{10} molecules

now connected to one extra oxygen as $-\overset{\diagdown}{\underset{\diagup}{P}} \rightarrow O$. This P—O distance (1.39A) is very short compared to the other P—O (1.62A). Single bond covalent radius gives a P—O distance of 1.06 + 0.66 = 1.72A. Thus a *p*π(O)—*d*π(P) double bonding via π-overlap of a filled *p*-orbital of oxygen with a vacant *d*-orbital of the phosphorus occurs (Fig. 18.3 (*a*) and (*b*)).

18.5.7. Oxyacids of Phosphorus : Compared to the oxyacids of nitrogen, phosphorus presents a much more complicated picture particularly due to the formation of condensed phosphates. Phosphorus forms oxyacids in the oxidation numbers + 1, + 3, + 4 and + 5. The oxyacids with oxidation numbers + 3 and + 5 occur in meta-, pyro- and ortho-forms (Table 18.6). The three oxyacids H_3PO_2, H_3PO_3 and H_3PO_4 are based on sp^3 hybridised phosphorus and may be conceived to be formed from hypophosphorus acid by stepwise replacement of H by OH (18-XIII: 18-XIV); 18-XV):


(18-XIII)


(18-XIV)


(18-XV)

Overlap of the four sp^3 hybrid orbitals of phosphorous each containing one electron with suitable orbitals of hydrogen and oxygen gives four σ-bonds. The fifth phosphorus electron is assumed to be in a *d*-orbital which can overlap with another unpaired electron of the oxo-oxygen making a *d*π—*p*π bond. This bonding scheme is supported by an appreciable multiple character of the P—O bonds of the acid anions. When the hydrogen connected to the hydroxy oxygen dissociates to form the anion, all the oxygens become equivalent. Note that those hydrogens bound covalently to the phosphorus (which is as much electronegative as hydrogen) are not ionisable but those linked to oxygen are. Therefore H_3PO_2 is monobasic, H_3PO_3 is dibasic and H_3PO_4 is a tribasic acid. The relative strengths of these acids have been discussed in Chapter 8.

Table 18.6. Oxyacids of Phosphorus

Oxidation Number	Oxyacid	Ortho-, meta-and para-forms
+ 1	H_3PO_2 (hypophosphorous acid)	—
+ 3	H_3PO_3 (phosphorous acid)	H_3PO_3,HPO_2 and $H_4P_2O_5$
+ 4	$H_4P_2O_6$ (hypophosphoric acid)	—
+ 5	H_3PO_4 (phosphoric acid)	H_3PO_4, HPO_3 and $H_4P_2O_7$

Hypophosphorous Acid: The sodium salt is formed on boiling white phosphorus with NaOH solution. Baryta gives the barium salt which on treatment with sulphuric acid provides the free acid. It forms colourless crystals (M.P. 27°C).

$$P_4 + 3H_2O + 3NaOH \rightarrow PH_3 + 3NaH_2PO_2$$

$$Ba(H_2PO_2)_2 + H_2SO_4 \rightarrow BaSO_4 + 2H_3PO_2$$

The acid is weak ($K_A \sim 10^{-2}$). It is a powerful reducing agent. It is oxidised in air to phosphorous acid and then to phosphoric acid.

$$H_3PO_2 + 4AgNO_3 + 2H_2O \rightarrow 4Ag + H_3PO_4 + 4HNO_3$$

$$3H_3PO_2 + 2CuSO_4 + 3H_2O \rightarrow 2CuH + 3H_3PO_2 + 2H_2SO_4$$

$$H_3PO_2 + O_2 \rightarrow H_3PO_4$$

Phosphorous Acid: The simplest method of its synthesis consists in passing chlorine through phosphorus kept fused under water. The phosphorus trichloride formed is immediately hydrolysed. The solution is evaporated and allowed to cool when the acid crystallises (M.P. ~ 70°C).

$$2P + 3Cl_2 \rightarrow 2PCl_3 \;;\; PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

This is a weak dibasic acid ($K_A^I \sim 10^{-2}$). It is a weaker reducing agent than H_3PO_2. The pyro- and meta-phosphorous acids may be viewed to be formed as a result of dehydration of phosphorous acid.

$$\begin{tikzcd}
2H_3PO_3 \arrow[r, "\text{gentle heat, } -H_2O"] & \underset{\text{(pyro)}}{H_4P_2O_5} \arrow[d, "\text{strong heat } (-H_2O)"] \\
H_3PO_3 \arrow[r, "\text{strong heat, } -H_2O"] & \underset{\text{(meta)}}{HPO_2}
\end{tikzcd}$$

A route to the synthesis of the pyro- and the meta-acids is controlled heating of phosphorous acid.

Phosphoric Acid: It is made by dissolving P_4O_{10} in water.

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

Phosphoric acid of commerce is manufactured by the action of dilute sulphuric acid on powdered phosphate rock or bone ash, the calcium sulphate being recovered as gypsum.

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3CaSO_4.2H_2O$$

The reaction is carried out in lead-lined tanks provided with stirring device. Gypsum is allowed to settle and the phosphoric acid solution is collected. Alternatively phosphate rock, silica and coke are treated in an electric arc furnace whereby white phosphorus vapour is set free.

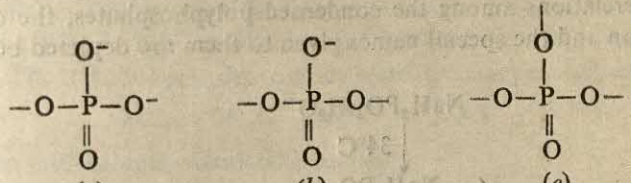
$$2Ca_3(PO_4)_2 + 6SiO_2 \rightarrow 6CaSiO_3 + P_4O_{10}$$

$$P_4O_{10} + 10C \rightarrow P_4 + 10CO$$

The phosphorus vapour is mixed with air to make P_4O_{10} which is then absorbed in water. It is usually sold as syrupy phosphoric acid (85% solution). The pure acid is a colourless solid (M.P. ~ 43°C). This is obtained by the removal of water from syrupy phosphoric acid under reduced pressure. It is a weak tribasic acid and has no reducing or oxidising properties. Stepwise hydrolysis of P_4O_{10} or conversely stepwise dehydration of H_3PO_4 gives the pyro- and meta-phosphoric acid.

$$H_3PO_4 \xrightarrow{\text{gentle heat}} H_4P_2O_6 \xrightarrow{\text{strong heat}} HPO_3$$

Chemistry of phosphoric acid and phosphates is much complicated because of the varied condensations that occur. Condensed phosphates contain more than one P atom and have P—O—P links. Condensed phosphates may have the PO_4 tetrahedra joined through one, two or three —O— atoms, the double bonded oxygen not participating in the condensation (18-XVI; *a*, *b*, *c*).

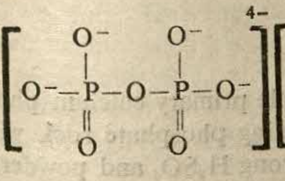


(*a*) (*b*) (*c*)

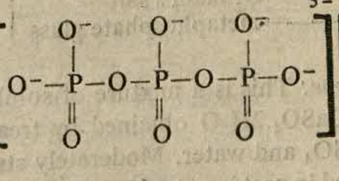
(18-XVI)

Isopolyacids of phosphorus: Isopolyacid is an acid the anion of which contains more than one acid group of the same kind. Isopolyacids of phosphorus are varied in nature.

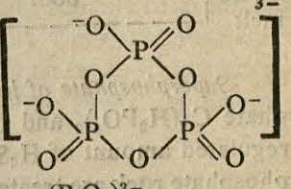
The extension of the phosphate tetrahedra may give linear as also cyclic polyphosphates. Linear polyphosphates have the general formula $(P_nO_{3n+1})^{(n+2)-}$ common examples being the pyrophosphates $M_4{}^1P_2O_7$ (18—XVII) and $M_5{}^1P_3O_{10}$ (18—XVIII). The first one is a dipolyphosphate and the second a tripolyphosphate. Cyclic polyphosphates have the general formula $[P_nO_{3n}[^{n-}$, $M_3P_3O_9$ a trimetaphosphate being an example (18—XIX):



$(P_2O_7)^{4-}$
(18—XVII)



$(P_3O_{10})^{5-}$
(18—XVIII)



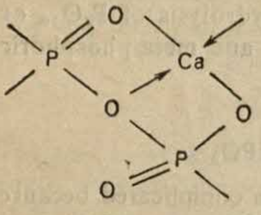
$(P_3O_9)^{3-}$
(18—XIX)

Complicated sets of condensed polyphosphates can be synthesised by changing reaction conditions. Orthophosphates undergo different degrees of condensation on being heated:

$$NaH_2PO_4 \xrightarrow{160°C} Na_2H_2P_2O_7 \xrightarrow{240°C} Na_3P_3O_9 \xrightarrow{650°C} (NaPO_3)x$$

$$Na_2HPO_4 \xrightarrow{450°C} Na_5P_3O_{10}$$

Such reactions produce, in general, more than one type of phosphate. These are usually separated by ion-exchange or chromatographic technique. Many of these condensed phosphates are of commercial importance. Sodium hexameta-phosphate under a technical name *calgon** is widely used as a water softener. It is obtained by heating microcosmic salt:

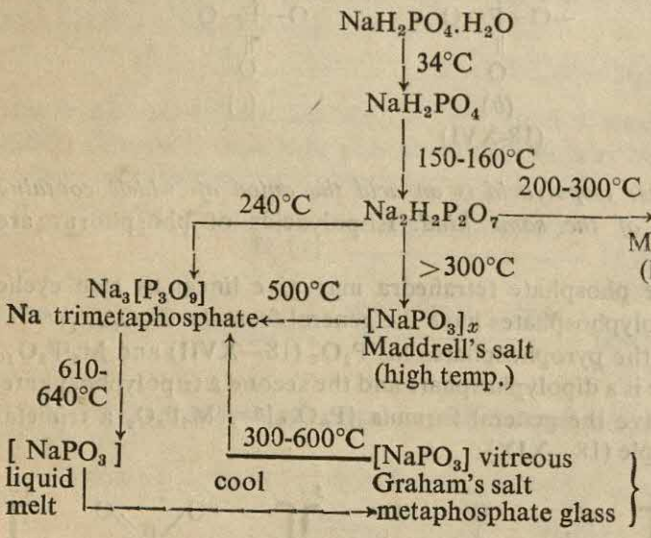


(18-XX)

$$NaNH_4HPO_4 \rightarrow NaPO_3 + NH_3 + H_2O$$

The molten metaphosphate is rapidly cooled. It is a hexamer $(NaPO_3)_6$, a cyclic polyphosphate. It binds calcium ion in the form of a complex ion of unknown composition and thereby prevents it from forming a precipitate with soap. The linking of Ca^{2+} may be somewhat like (18-XX).

The interrelations among the condensed polyphosphates, the conditions of their formation and the special names given to them are depicted below:



Superphosphate of lime: This is a mixture of soluble primary calcium phosphate $Ca(H_2PO_4)_2$ and $CaSO_4.2H_2O$ obtained by treating phosphate rock with regulated amount of H_2SO_4 and water. Moderately strong H_2SO_4 and powdered phosphate rock are treated in cast iron tanks provided with charge inlet, gas outlet and a stirring device. The major reaction is:

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 2H_2O \rightarrow Ca(H_2PO_4)_2 + 2CaSO_4.2H_2O$$

But HF (from CaF_2 in the rock), SiF_4 (from CaF_2 and silica), CO_2 (from limestone) etc. are also evolved. These by-products may be recovered as sodium fluoride, sodium silicofluoride etc. Superphosphate is a good fertiliser since it is soluble in water and therefore more readily assimilable by plants.

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* Calgon' meaning 'calcium gone'

18.5.8. Halides of Phosphorus : Several mononuclear trihalides and pentahalides are known: PF_3 (B.P.−95°C); PCl_3 (B.P. 76°C); PBr_3 (B. P. 173°C); PI_3 (M.P. 61°C); PF_5 (B.P.−75°C); PCl_5 (sulbimes 163°C) and PBr_5 (M.P. 100°C). Some dinuclear halides are also known: P_2Cl_4 (B.P. 180°C) and P_2I_4 (M.P. 124°C). Some mixed halides such as PF_2Cl, $PFCl_2$, PF_2Br, etc. have also been reported. Note that in conformity with our generalisations on the boiling points of closely related covalent compounds, the boiling points of the halides are functions of their molecular weights.

The general approach to their syntheses involves for the trihalides reaction of the halogens with excess phosphorus and for the pentahalides reaction of phosphorus with excess halogens. For PCl_3, dry white phosphorus is placed in a retort on a sand bath. Into the retort is led a stream of dry chlorine. The height of the chlorine delivery tube above the phosphorus bed is so adjusted that neither phosphorus distills (as occurs when the delivery tube is very close) nor much PCl_5 is formed. The PCl_3 is condensed and then purified from PCl_5 contaminant by distillation. The trihalide is hydrolysed by water to phosphorous acid:

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

With oxygen and halogens oxidation occurs:

$$2PCl_3 + O_2 \rightarrow 2POCl_3 \ ; \ PCl_3 + Cl_2 \rightarrow PCl_5$$

Fluorination of PCl_3 gives PF_3: $2PCl_3 + 3CaF_2 \rightarrow 2PF_3 + 3CaCl_2$.

All the trihalides are pyramidal (three sp^3 orbitals overlapping with three halogen orbitals and the fourth sp^3 housing the lone pair). They function as Lewis bases in complexes. By virtue of their having vacant *d*-orbitals they can also receive back donated electrons from low oxidation state metals:

$$Ni(CO)_4 + 4PCl_3 \rightarrow Ni(PCl_3)_4 + 4CO$$

Their capacity to function as Lewis acid is shown in $Me_3N \rightarrow PCl_3$.

The pentahalides have trigonal bipyramidal structures and have no lone pair of electrons. Thus they cannot act as donors. But they are capable of expanding their valence shell because of the availability of *d*-orbitals. They therefore serve as good Lewis acids, and react with halides, amines and other bases to form octahedral (sp^3d^2) complexes e.g. $[PF_6]^-$. Pentahalides are hydrolysed to phosphoric acid through the intermediate formation of $POCl_3$:

$$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl \ ; \ POCl_3 + 3H_2O \rightarrow H_3PO_4 + 3HCl$$

18.5.9. Hydrides of Arsenic, Antimony and Bismuth: Calcium arsenide (prepared by the union of calcium metal with arsenic) can be hydrolysed by water to give arsine. An alloy of zinc and antimony on treatment with dilute acid gives stibine. Treatment of a finely divided mixture of bismuth and magnesium with acid gives bismuthine. Besides the above hydrolytic approach, the hydrides may also be prepared by chemical reduction (by metallic Mg or Al or Zn) or by electrolytic reduction of trivalent arsenic, antimony or bismuth compounds.

These hydrides are all strong reducing agents, precipitating many heavy metals from their solutions. The hydrides are thermally unstable giving a deposit of the respective element. Marsh test for arsenic is based on the thermal decomposition of AsH_3.

18.5.10. Oxides of Arsenic, Antimony and Bismuth: Arsenic trioxide, correctly written as As_4O_6, resembles P_4O_6 in its synthesis, reaction towards water and in structure. Antimony oxide Sb_4O_6 also shows such similarities with P_4O_6. These oxides dissolve in alkalies to give salts of arsenious and antimonous acids, called arsenites and antimonites (Na_3AsO_3 or $NaAsO_2$; Na_3SbO_3 or $NaSbO_2$). The pentoxides are obtained by oxidising arsenic or antimony oxide with HNO_3 followed by dehydration of the acid by heating:

$$As_4O_6 + 8HNO_3 + 2H_2O \rightarrow 4H_3AsO_4 + 8NO_2;\ 2As_2O_5 + 6H_2O$$

Bismuth trioxide is obtained by burning the metal in air or better by heating bismuth oxynitrate:

$$4Bi + 3O_2 \rightarrow 2Bi_2O_3\ ;\ 4BiONO_3 \rightarrow 2Bi_2O_3 + 4NO_2 + O_2$$

It works as a basic oxide giving bismuth (III) salts such as the perchlorate, sulphate, nitrate etc via reaction with appropriate acids. Not much is known about bismuth (V) oxide.

18.5.11. Oxyacids of Arsenic, Antimony and Bismuth : Arsenious acid is not well established. It is more like hydrated arsenous oxide $As_4O_6.xH_2O$. *Sodium arsenite* is obtained by dissolving As_4O_6 in sodium hydroxide or in sodium bicarbonate:

$$As_4O_6 + 12NaHCO_3 \rightarrow 4Na_3AsO_3 + 6H_2O + 12CO_2$$

On evaporation the sodium salt crystallises. Arsenites are reducing agents, being oxidised to arsenates:

$$AsO_3^{3-} + 2Fe^{3+} + H_2O \rightarrow AsO_4^{3-} + 2Fe^{2+} + 2H^+$$
$$AsO_3^{3-} + I_2 + H_2O \rightleftharpoons AsO_4^{3-} + 2I^- + 2H^+$$

This reaction is a reversible one and may be forced to proceed to completion only if the liberated H^+ is removed quickly. This condition is best achieved by using a buffer solution of pH ~ 6.5 (0.1*N* sodium bicarbonate solution saturated with CO_2). Use of Na_2CO_3 or NaOH is not recommended as these react with iodine to form iodide, iodate, and hypoiodite.

Arsenic acid is usually made by boiling As_4O_6 with concentrated nitric acid:

$$As_4O_6 + 8HNO_3 + 2H_2O \rightarrow 4H_3AsO_4 + 8NO_2$$

A concentrated solution deposits crystals of $H_2AsO_4.\frac{1}{2}H_2O$. Arsenic acid is an oxidising agent:

$$AsO_4^{3-} + 2I^- + 2H^+ \rightarrow AsO_3^{3-} + I_2 + H_2O$$

It is a weak tribasic acid with $K^1_A \sim 10^{-2}$. Arsenates behave like phosphates.

Antimonous acid is not known. Antimonous oxide on reaction with alkalies give antimonites. But unlike the arsenates the antimonates mostly assume an octahedral geometry e.g. $Na[Sb(OH)_6]$, $K[Sb(OH)_6]$, $[Co(NH_3)_6]\,[Sb(OH_6)]_3.3H_2O$ Antimony pentoxide is obtained, like As_2O_5, by treating the lower oxide with nitric acid, evaporating the solution and igniting the residue. Antimony pentachloride also hydrolyses to give the pentoxide. The oxide dissolves in alkalies to give *antimonates:*

$$Sb_4O_6 + 8HNO_3 \rightarrow 2Sb_2O_5 + 8NO_2 + 4H_2O$$

$$2SbCl_5 + 5H_2O \rightarrow Sb_2O_5 + 10HCl$$

$$Sb_2O_5 + 2NaOH + 5H_2O \rightarrow 2Na[Sb(OH)_6]$$

Lower oxyacid is not known for bismuth. The higher oxyacid is known only in the form of alkali *bismuthate* salts. On fusing bismuth trioxide with alkali in air, a brown product of alkali bismuthate is obtained. Heating Bi_2O_3 with sodium peroxide also gives the bismuthate $NaBiO_3$. Bismuthates have not been obtained in a state of high purity. However bismuthates are strong oxidants and are used in the laboratory for oxidising manganese (II) to permanganate in acid solution:

$$2Mn^{2+} + 5BiO_3^- + 14H^+ \rightarrow 2MnO_4^- + 5Bi^{3+} + 7H_2O$$

or, $$2Mn^{2+} + 5BiO_3^- + 4H^+ \rightarrow 2MnO_4^- + 5BiO^+ + 2H_2O$$

Note that $NaBiO_3$ is very sparingly soluble in water.

18.5.12. Halides of Arsenic, Antimony and Bismuth: Table 18.7 shows that the trend towards higher pentahalides markedly falls from fluorine to iodine. This must be attributed to a special feature in the chemistry of fluorine. By virtue of its extreme electronegativity, small size and oxidising ability it helps other elements to attain their highest oxidation number and coordination number.

Table 18.7. Halides of Arsenic, Antimony and Bismuth

Element	F	Cl	Br	I
As	AsF_3 AsF_5	$AsCl_3$	$AsBr_3$	AsI_3
Sb	SbF_3 SbF_5	$SbCl_3$ $SbCl_5$	$SbBr_3$	SbI_3
Bi	BiF_3 BiF_5	$BiCl_3$	$BiBr_3$	BiI_3

Methods of syntheses are those applied to phosphorus pentahalides. Some of these methods are indicated below:

$$2As + 3Cl_2 \rightarrow 2AsCl_3\ \text{(liquid)}$$

$$As_4O_6 + 6CaF_2 + 6H_2SO_4 \rightarrow 4AsF_3 + 6CaSO_4 + 6H_2O$$

$$2As + 5F_2 \rightarrow 2AsF_5(+ \text{little liquid } AsF_3)$$
$$2As + 3Br_2 \text{ (in } CS_2) \rightarrow 2AsBr_3$$
$$Sb_4O_6 + 12HF \rightarrow 4SbF_3 + 6H_2O$$
$$Bi_2O_3 + 6HF \rightarrow 2BiF_3 + 3H_2O$$
$$2Bi + 3F_2 \rightarrow 2BiF_3 \xrightarrow[600°C]{F_2} BiF_5$$
$$SbCl_3 + Cl_2 \rightarrow SbCl_5$$

Our general conclusions on phosphorous halides also stand for the halides of arsenic, antimony and bismuth. The trihalides are volatile, are readily hydrolysed and are pyramidal (sp^3 hybridisation of the central atom with a lone pair occupying one orbital). Unlike PX_3 molecules, the halides of As, Sb and Bi can add on extra halide ions giving halo complexes such as $[BiCl_6]^{3-}$, $[SbF_5]^{2-}$, $[SbCl_6]^{3-}$ etc. The pentahalides are strong Lewis acids and can form complexes with amines, ethers and suitable bases (that is with Lewis donors). Antimony pentachloride is a powerful chlorinating agent, and bismuth pentafluoride is a powerful fluorinating agent. The increase in base character from arsenic to bismuth is revealed by the properties of BiF_3. It has all the characteristics of a salt. It is a white powder which shows no volatility even at red heat.

18.5.13. Phosphonitrilic Compounds: These are a class of compounds containing phosphorus-nitrogen rings alongwith halide groups attached to phosphorus. They may be viewed as made up of tri-covalent nitrogen and pentacovalent phosphorus. Some typical syntheses are shown below:

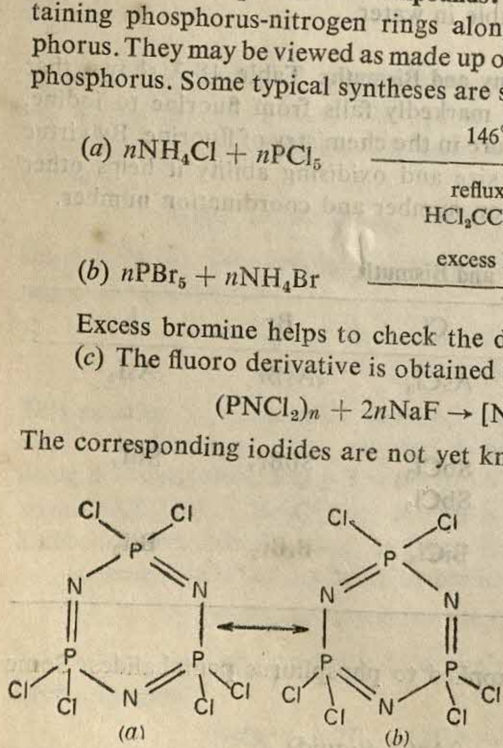
(*a*) $$n NH_4Cl + n PCl_5 \xrightarrow[\text{reflux in } HCl_2CCHCl_2]{146°} (PNCl_2)_n$$

(*b*) $$n PBr_5 + n NH_4Br \xrightarrow{\text{excess } Br_2} (PNBr_2)_n$$

Excess bromine helps to check the decomposition of PBr_5 to PBr_3 and Br_2.
(*c*) The fluoro derivative is obtained from the chloride:

$$(PNCl_2)_n + 2n NaF \rightarrow [NPF_2]_n + 2n NaCl$$

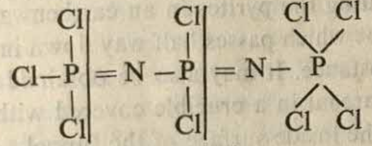
The corresponding iodides are not yet known. The trimers ($n = 3$) possess the best stability. Their structures involve sp^2 hybridized trivalent nitrogen and roughly sp^3 hybridised pentavalent phosphorus. Alternate double bond and single bond are present between nitrogen and phosphorus in the planar ring (18-XXI ; *a* ; *b*). Through resonance all the P–N distances are the same (1.67A) and are less than the expected P–N



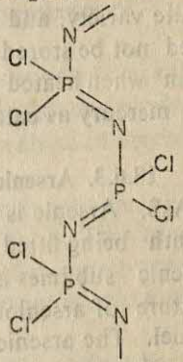
(18-XXI)

single bond (1.78A). Unlike borazole or benzene the π-bonds in the ring involve *p*-orbitals of nitrogen and *d*-orbitals of phosphorus.

When excess PCl_5 is used in the reaction (*a*) above linear polymers of the following type (18–XXII) are obtained. They are rubbery in nature, have some elasticity and thermal stability but are very sensitive to hydrolytic degradation. Another type of long chain compound $(PNCl_2)_x$ is obtained by heating $(PNCl_2)_3$ to 250–350°C to give products of molecular weight of 20,000 or more. This type is believed to have structure (18–XXIII). The end groups of these high molecular weight substances are not definitely known. These rubbery substances are also called *inorganic rubber*.



(18-XXII)



(18-XXIII)

18.6. ISOLATION OF THE GROUP VB ELEMENTS

18.6.1. Nitrogen: On commercial scale nitrogen is obtained by liquefaction of air, the liquid air being fractionally distilled. Nitrogen being lower boiling (–196°C) than oxygen (–183°C) comes off earlier but remains admixed with some oxygen as also with some argon (B.P.–187°C). The admixed oxygen can be removed in a variety of ways: by combining with H_2 over a platinum catalyst, by absorbing over heated copper or in a solution of a strong reducing agent such as V^{2+} or Cr^{2+}. Molecular nitrogen is very inert due to an extremely stable triple bond.

18.6.2. Phosphorus: Phosphorus occurs in nature as *phosphorite* $(Ca_3(PO_4)_2)$, *fluorapatite* $(3Ca_3(PO_4)_2.CaF_2)$ and *chlorapatite* $(3Ca_3(PO_4)_2.CaCl_2)$. Most of the phosphorus rocks are worked for the manufacture of the soluble calcium phosphate. $Ca(H_2PO_4)_2$, called *superphosphate of lime*. Only about 10% of the annual work-up of the phosphate rock is used to make elementary phosphorus and other phosphorus compounds.

White phosphorus (P_4) is obtained by heating a mixture of phosphorite, silica and coke in an electric arc furnace at ~3000°C. Phosphorus vapourises and leaves the furnace through an exit at the top. It is condensed by cooling in cold water and cast into sticks and stored under water. The fusible calcium silicate is removed through a slag hole.

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \rightarrow P_4 + 6CaSiO_3 + 10CO$$

White phosphorus changes to a red variety on heating in an inert (N_2/CO_2) atmosphere for several hours around 250°C. The transformation is exothermic and might often be explosive. The resulting mass containing some unchanged white phosphorus is ground under water, boiled with a solution of alkali to remove the white phosphorus and finally washed and dried. It is far less reactive than the white variety, and its structure is uncertain. The red variety is stable to air and need not be stored under water. White phosphorus changes to a black crystalline form when heated under high pressure or at 220–350°C for a week in the presence of mercury as catalyst and with little black phosphorus as seed.

18.6.3. Arsenic: Commonest source of arsenic is arsenical pyrites (*mispickel*), FeAsS. Arsenic is obtained by heating the pyrites in an earthenware retort, the mouth being fitted with an iron tube which passes half way down into the retort. Arsenic sublimes as a lustrous substance. It may also be obtained by heating a mixture of arsenious oxide and charcoal in a crucible covered with an inverted funnel. The arsenic condenses on the inside surface of the funnel.

$$\mathrm{FeSAs \rightarrow FeS + As \;;\quad As_4O_6 + 6C \rightarrow 4As + 6CO}$$

18.6.4. Antimony: Antimony is found in nature mostly in the form of *stibnite* Sb_2S_3. The element can be extracted by heating the ore in fireclay pots with perforated bottoms. Antimony sulphide melts and trickles out of the pot. The sulphide is then reduced by heating with scrap iron in graphite pots. Fused antimony forms a layer and is tapped off:

$$\mathrm{Sb_2S_3 + 3Fe \rightarrow 3FeS + 2Sb}$$

Alternatively poor quality stibnite is roasted to give Sb_2O_3. The volatile oxide is condensed as solid. The oxide is then reduced by carbon in crucibles:

$$\mathrm{Sb_2O_2 + 3C \rightarrow 2Sb + 3CO}$$

18.6.5. Bismuth: Important sources of bismuth are *bismuth ochre* (Bi_2O_3), *bismuth glance* (Bi_2S_3) and *bismuth carbonate* $(BiO)_2CO_3$. The ore is first roasted to Bi_2O_3 which is then reduced by carbon:

$$\mathrm{2Bi_2S_3 + 9O_2 \rightarrow 2Bi_2O_3 + 6SiO_2}$$

$$\mathrm{(BiO)_2CO_3 \rightarrow Bi_2O_3 + CO_2}$$

$$\mathrm{Bi_2O_3 + 3C \rightarrow 2Bi + 3CO}$$

18.7. USES OF THE GROUP VB ELEMENTS

Nitrogen is used in the manufacture of ammonia and of calcium cyanamide. Bulbs of incandescent lamps are filled with a mixture of nitrogen and argon, or by argon alone. It is used in the laboratory to provide an inert atmosphere.

Phosphorus is used in the manufacture of safety matches. The tip of a matchstick contains antimony sulphide, Sb_2S_3, which can be ignited during an oxidation-reduction reaction with substances such as lead dioxide or potassium chlorate. The match head contains a mixture of antimony sulphide and lead dioxide (or potassium chlorate or potassium chromate). The side of a match box is coated with a mixture of glue, an abrasive and red phosphorus. When the match is struck a trace of the red phosphorus gets ignited, and this sets fire to the match stick. Phosphorus finds application in the manufacture of certain types of bronzes, white phosphorus finds use as a rat poison, and as the source of syntheses of other phosphorus compounds.

Arsenic is used in the manufacture of certain types of bronzes as well as other varieties of alloys. Its presence increases the fluidity, lustre, strength and hardness of the alloys. Arsenic compounds find use for their toxicity such as in arsenical insecticide.

Antimony is widely used in lead storage batteries. Antimony-containing lead is harder than ordinary lead, and is more resistant to acids. This quality makes it suitable for the construction of lead antimony plates of storage batteries. Antimony-lead alloy is used for bullets and bearings. *Type metal* is also a lead-tin-antimony alloy (60% Pb; 30% Sb; 10% Sn).

Bismuth finds application in the manufacture of low-melting alloys for use in electric fuses, automatic fire alarms, safety plugs on boilers etc. Woods' metal (50% Bi, 25% Pb, 12.5% Sn and 12.5% Cd) has a melting point ~71°C. Bismuth salts find use in pharmaceutical preparations.

18.8. ANALYTICAL REACTIONS OF THE GROUP VB ELEMENTS

Nitrogen content of a compound can be determined by converting the compound into ammonium sulphate by digesting with concentrated sulphuric acid in the presence of potassium bisulphate, copper sulphate and selenium. The solution is then made strongly alkaline, boiled in the presence of little zinc dust and the liberated ammonia absorbed into an excess of standard acid. The remaining acid is back titrated with an alkali solution. This determination known as the Kjeldahl method is not suitable for compounds containing heterocyclic nitrogen, since such compounds are not easily transformed to ammonium salts. In such situation nitrogen content is determined by Dumas' combustion technique. The sample is mixed with fine copper oxide powder and ignited in an atmosphere of pure CO_2. The evolved gases are allowed to pass through a packing of copper oxide and copper gauze (at 700°C) and then led through 50% KOH solution. Nitrogen alone is collected, and all other gases react with copper oxide, copper gauze or KOH.

Phosphorus may be detected by heating the substance with a few pieces of magnesium ribbon whereby magnesium phosphide, Mg_3P_2, is formed. When this is treated with water PH_3 is evolved, which can be detected by its characteristic smell. Phosphoric acid and phosphates are generally detected by the yellow precipitate of phosphomolybdate $(NH_4)_2H[PO_4(MoO_3)_{12}]$, a heteropolyacid, obtained on the addition of ammonium molybdate in the presence of concentrated HNO_3:

$$12(NH_4)_2MoO_4 + (NH_4)_3PO_4 + 25HNO_3 \rightarrow (NH_4)_2H[PO_4(MoO_3)_{12}] + 25NH_4NO_3 + 12H_2O$$

On washing with ammonia the precipitate becomes $(NH_4)_3[PO_4(MoO_3)_{12}]$. For quantitative estimation phosphate may be precipitated as $Mg(NH_4)PO_4.6H_2O$

from slightly ammoniacal solutions. The precipitate is ignited to $Mg_2P_2O_7$ and weighed.

Traces of *arsenic* may be detected by making use of the easy thermal decomposition of its hydride AsH_3 to give a mirror of elementary arsenic. This extremely sensitive test, known as Marsh test, is used in forensic laboratories. An arsenic compound on reduction with Zn and H_2SO_4 evolves AsH_3, which can then be decomposed by passing through a heated tube:

$$AsO_3^{3-} + 9H^+ + 3Zn \rightarrow AsH_3 + 3Zn^{2+} + 3H_2O \text{ ; } 2AsH_3 \rightarrow 2As + 3H_2$$

It is precipitated as the sulphide, As_2S_3, in group IIB of the qualitative scheme. The sulphide dissolves in yellow ammonium sulphide to form soluble thioarsenate:

$$As_2S_3 + 3S^{2-} + 2S \rightarrow 2[AsS_4]^{3-}$$

Acidification of thioarsenate gives arsenic pentasulphide. Arsenic (III) can be readily oxidised to arsenates by nitric acid, and can be precipitated as $Mg(NH_4)AsO_4.6H_2O$. The precipitate can be ignited to $Mg_2As_2O_7$ and weighed.

Antimony salts are precipitated as sulphides in group IIB. The precipitate also dissolves in ammonium polysulphide to give thioantimonate. It is distinguished from arsenic sulphide by its colour (orange as against yellow of As_2S_3), its insolubility in ammonium carbonate solution and its solubility in concentrated HCl. Antimony compounds also give antimony mirror via thermal decomposition of its hydride SbH_3. The arsenic mirror dissolves in sodium hypochlorite (or sodium hydroxide plus hydrogen peroxide) but the antimony mirror remains unchanged. Antimony may be determined as Sb_2S_3 after drying at 280—300°C in CO_2 atmosphere. Trivalent antimony (also arsenic) can also be determined by titration against permanganate or against iodine solution:

$$4MnO_4^- + 5Sb_2O_3 + 12H^+ \rightarrow 4Mn^{2+} + 5Sb_2O_5 + 6H_2O$$

$$Sb_2O_3 + 2I_2 + 2H_2O \rightarrow Sb_2O_5 + 4H^+ + 4I^-$$

Bismuth is precipitated by H_2S as brown Bi_2S_3. This is insoluble in ammonium sulphide but dissolves in nitric acid. On dilution with water bismuth salts precipitate oxysalts, which is often utilised as a test for bismuth. Antimony salts also give precipitate on dilution. Bismuth is quantitatively determined by precipitating and weighing as BiOI, and also by precipitation as cupferron complex from slightly ammoniacal solution and igniting to Bi_2O_3. Bismuth may also be precipitated as $[Bi(oxin)_3]$ from neutral solution and weighed as such.

STUDY QUESTIONS

1. Compare the elements nitrogen, phosphorus, arsenic, antimony and bismuth with regard to the following: (*a*) electronic configurations, (*b*) ionisation potential and electronegativity and (*c*) acidic and basic properties.
2. Present a concise account of the oxides and oxyacids of phosphorus.
3. Discuss the structure and chemical behaviour of nitric oxide.
4. Phosphorus becomes a good electrical conductor under high pressure. Comment.
5. The hydrolysis of NCl_3 gives NH_3 and HOCl but NF_3 is very stable. Comment on the reaction.

6. Phosphorus chemistry is closer to arsenic chemistry than to nitrogen chemistry. Discuss.

7. Give an account of the XH_3 hydrides (X = N, P, As, Sb, Bi) of this group.

8. Compare HNO_2 and HNO_3 in regard to: (*a*) strength as acids, (*b*) oxidation state of nitrogen, (*c*) ability to act as oxidant and reductant and (*d*) structure of their ions.

9. Both HCl and HNO_3 are strong acids. But copper dissolves in HNO_3 but not in HCl. Explain.

10. The differences in the chemistries of nitrogen and phosphorus are largely due to phosphorus having *d*-orbitals. Comment.

11. How can antimonate ion have the formula $[Sb(OH)_6]^-$ while arsenate ion is AsO_4^{3-} ?

12. Discuss the methods for qualitative detection and quantitative estimation of P, As, Sb and Bi.

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19

Group VIB. Oxygen, Sulphur, Selenium, Tellurium and Polonium

This group has as its members oxygen, sulphur, selenium, tellurium and polonium. Oxygen is the most abundant of elements and makes up ~ 47% of the earth's crust in the form of oxides and oxysalts. It occurs to ~ 21% by volume in air, and to ~ 86% by weight in oceans. Natural oxygen is an isotopic mixture of O-16, O-17 and O-18. Oxygen supports respiration and is essential for life. A grown-up person consumes ~ 20 litres of oxygen per hour. Sulphur occurs in the native state in considerable amount and also in the form of metal sulphides (*pyrites*, FeS_2; *galena*, PbS; *zinc blende*, ZnS etc.) and metal sulphates (*gypsum*, $CaSO_4.2H_2O$; *epsom salt*, $MgSO_4.7H_2O$; *celestine*, $SrSO_4$ etc.). Sulphur makes up ~ 0.04−0.03% of the earth's crust and oceans have a sulphur content of ~ 0.09% in the form of sulphates. Selenium occurs in trace quantities (0.00006%) and accompanies sulphide ores as metal selenides. Tellurium is even less common and occurs as minor constituents of sulphide ores. Polonium was discovered by the Curies from pitchblende in 1898. This is a decay product of radium and like radium is also an alpha emitter.

Oxygen, sulphur, selenium and tellurium are often collectively called as *chalcogens*.

19.1. COMPARATIVE STUDY OF THE GROUP VIB ELEMENTS

19.1.1. General Considerations: The outermost quantum shell of oxygen, sulphur, selenium, tellurium and polonium consists of the s^2p^4 electronic configuration. Oxygen alone does not possess any *d*-orbital since its $n = 2$ quantum shell cannot have any. Oxygen cannot therefore show a valence beyond 2 as it cannot expand its valence shell beyond an octet. But the other elements of the group can use their vacant *d*-orbitals for bonding purposes giving valences 2, 4 and 6.

The ionisation potentials (Table 19.1) are in general high but expectedly they decrease down the group. That metallic character is favoured with increasing atomic number is shown by a decrease in the resistance of the elements: sulphur is an insulator, selenium and tellurium are semiconductors and polonium a metal. Specific resistances are: S(10^{23}); Se(10^{11}); Te(10^{5}) and ~ Po(40) micro ohms cm.

Table 19.1. Electronic Configurations and Some Properties of Group VIB Elements

Element	Atomic Number	Electronic Configuration	Ionisation Potential (*ev*)	Electro-negativity
Oxygen	8	[He] $2s^2 2p^4$	13.6, 35.11, 54.89, 77.39 113.87	3.5
Sulphur	16	[Ne] $3s^2 3p^4$	10.36, 23.4, 35.0, 47.29, 72.5	2.5
Selenium	34	[Ar] $3d^{10} 4s^2 4p^4$	9.75, 21.5, 32.0, 42.9, 68.3	2.4
Tellurium	52	[Kr] $4d^{10} 5s^2 5p^4$	9.01, 18.6, 31, 38.60	2.1
Polonium	84	[Xe] $4f^{14} 5d^{10} 6s^2 6p^4$	8.43.	

The elements are just two electrons short of the next noble gas configuration, which configuration can be achieved in several ways: (*a*) by gaining two electrons to form binegative ions (*chalcogenides* or *chalconides*, X^{2-}), (*b*) by making two single covalent bonds (—X—) or (*c*) by one double bond (= X). The trend in the formation of the divalent anions should be reflected in the electron affinities of the elements but these vary rather irregularly along the group. Important it is to note that although the first electron capture releases energy (conventionally taken as positive; Chapter 4) the overall affinity ($X + 2e \rightarrow X^{2-}$) is significantly negative. The formation of X^{2-} ions is thus unfavourable. In practice, however, many ionic compounds with oxides, sulphides, etc are known, their formation being possible through favourable lattice energies (Chapter 5). Electronegativity of oxygen is only next to that of fluorine, and the values of the other chalcogens decrease down the group. Oxides of metals are therefore more ionic than the other chalcogenides of the same metal. According to the SHAB principle (Chapter 8) the large anions being the more polarisable ones will prefer to bind strongly polarisable cations. So sulphides, selenides, tellurides being soft bases combine to give stabler compounds with soft acids (class '*b*' acceptors) such as Ag^+, Cu^+, Pd^{2+}, Pt^{2+}, Hg^{2+}, etc.

Table 19.2 records some other properties of the group VIB elements. Note that with increase in atomic number the atomic radii and ionic radii also increase.

Table 19.2. Some More Properties of Group VIB Elements

Element	Atomic Radius (A)	Ionic (X^{2-}) Radius (A)	M.P. (°C)	B.P. (°C)	Density (*g/ml*)
Oxygen	0.66	1.40	—219	—183	1.27
Sulphur	1.04	1.84	12.8*; 119+	445	2.06
Selenium	1.17	1.98	217	685	4.80
Tellurium	1.37	2.21	450	1390	6.24
Polonium	1.64	2.30	254	962	9.51

*rhombic form; + monoclinic form

19.1.2. Chemical Behaviour: *Hydrides:* All the elements form volatile covalent hydrides. Leaving aside H_2O, all the other hydrides H_2S, H_2Se, H_2Te follow the usual sequence of increasing boiling point with increasing molecular weight. H_2O is highly associated due to hydrogen bonding. The reducing properties of the hydrides increase down the group, this trend being due to their instability which again is connected with the size of the parent element. The acidity of the hydrides, contrary to expectation from electronegativity, increases from H_2O to H_2Te. The factors responsible for this anomalous behaviour have been discussed in Chapter 8. As the size of the central atom increases so also the distance between hydrogen and the central atom. Release of proton (acid behaviour) is thus favoured.

Hydride	H_2O	H_2S	H_2Se	H_2Te
K_A^1	1×10^{-14}	1×10^{-7}	1.7×10^{-4}	2.3×10^{-3}

Oxides and Oxyacids: Oxides are commonly classified from their acid—base behaviour as acidic, basic or amphoteric. Oxides of group IA/IIA elements are generally basic, oxides of group IV to VII elements are acidic, others being amphoteric. Many of the lower-valent metal oxides are ionic and form close packed systems, the metal ions occupying the holes created by the close packing of oxide ions. As the valence increases the oxides tend to be covalent (cf: Fajans' rules). The melting points of the oxides of group IA and those of group IIA metals fall down the group. This trend follows from Coulomb's law because structure type remaining the same (ionic) increasing cation-anion separation decreases the force between the ions (Chapter 5). Comparing the oxide, sulphide, selenide and telluride of the same metal ion it is observed that the heat of formation decreases from oxygen to tellurium. Small and highly charged cations (hard acids) prefer oxide ions to sulphide ions. The high valence states are rather easily reduced by sulphide ions.

The acidity of oxyacids of the same central element increases with increasing oxidation number: $H_2SO_3 < H_2SO_4$; $H_2SeO_3 < H_2SeO_4$ etc. This is the trend expected from electronegativity. With the same oxidation number acidity decreases down the series (Chapter 8 and Table 19.4).

Halides: Oxygen halides are all covalent and are restricted to a maximum of two halogens linked to one oxygen. These are of the type F—O—F or Cl—O—Cl or O—Cl—O. That one oxygen cannot bind more than two halogens must be linked with the inability of oxygen to expand its octet.

A number of hexahalides, tetrahalides and dihalides are known with S, Se and Te. In all cases combination with fluorine provides the highest halides. SF_6, SeF_6 and TeF_6 are volatile covalent molecules of low boiling points. They have octahedral (sp^3d^2) structures. SF_6 is very stable, SeF_6 is more reactive and TeF_6 is hydrolysed by water to HF and H_6TeO_6. Although all three S, Se and Te possess *d*-orbitals to assist nucleophilic attack by H_2O during hydrolysis, the weakness of Te—F bonds due to decreasing non-metal character of Te is probably responsible for its easy hydrolysis. The tetrahalides often act as Lewis bases (electron donors) as in $F_4S \rightarrow BF_3$ and sometimes as Lewis acids as in $H_2[SeCl_6]$. Note that the tetrahalides possess a valence shell of (6 + 4) 10 electrons. The dihalides have a valence shell of (6 + 2) 8 electrons. The tetrahalides have a trigonal bipyramid (sp^3d) structure, four positions being occupied by four halogens and the fifth by a lone pair. The dihalides have tetrahedral (sp^3) array of two halogens and two lone pairs.

Donor Properties: These elements in —X— or = X state possess lone pairs of electrons so that they may serve as ligands. Examples are $H_2O, R_2S, (C_6H_5)_3PO$, etc. Since oxygen does not possess *d*-orbitals but sulphur does, oxygen donors cannot stabilise low oxidation states of metals but sulphur donors can, by virtue of their ability to receive back donated electrons from low-valent metals into their *d*-orbitals. With heavier elements of this group non-metal character decreases and hence donor properties fall down the group. It may be recalled that nitrogen donors (such as NH_3, en) also cannot stabilise low oxidation states whereas trivalent P and As ligands can (Chapters 10 and 23).

19.2. ELEMENTARY FORMS OF THE GROUP VIB ELEMENTS

Oxygen is a diatomic molecule conventionally written with a double bond O = O having a p_x-p_x σ-bond and a p_y-p_y (or p_z-p_z)π bond. However this valence bond picture cannot explain the paramagnetism of the O_2 molecule. Molecular orbital theory of O_2 puts two unpaired electrons in the two π^* antibonding orbitals (Chapter 5):

$$O_2 \text{ M.O. electron distribution: } \frac{\uparrow\downarrow}{\sigma_{2s}} \quad \frac{\uparrow\downarrow}{\sigma^*_{2s}} \quad \frac{\uparrow\downarrow}{\sigma_{2px}} \quad \frac{\uparrow\downarrow}{\pi_{2py}} \quad \frac{\uparrow\downarrow}{\pi_{2pz}} \quad \frac{\uparrow}{\pi^*_{2py}} \quad \frac{\uparrow}{\pi^*_{2pz}}$$

Ozone is an interesting molecular allotropic form of oxygen. It is obtained by passing an electric discharge through oxygen or by the anodic oxidation of a concentrated aqueous solution of perchloric acid at −50°C. Under these conditions oxidation of water occurs at the anode and ozone is liberated. It is a blue gas freezing to a purple solid at ~ −193°C. Ozone is one of the strongest oxidants known. In acid solution the formal potential of the O_3/O_2 couple is 2.07 volts being lower than those of only $F_2/2F^-$, atomic oxygen/water and $F_2O/2F^-$ couples:

$$O_3 + 2H^+ + 2e \rightleftharpoons O_2 + H_2O;\ E^\circ = +2.07 \text{ volts}$$

$$O + 2H^+ + 2e \rightleftharpoons H_2O;\ E^\circ = +2.2 \text{ volts} : \ F_2O + 2H^+ + 4e \rightleftharpoons H_2O + 2F^-;\quad E^\circ = 2.1 \text{ volts.}$$

It oxidises silver (I) to silver (II) and is used in many organic oxidations. Some of the oxidising reactions of ozone are recorded below:

$$PbS + 4O_3 \rightarrow PbSO_4 + 4O_2\uparrow$$

$$2FeSO_4 + H_2SO_4 + O_3 \rightarrow Fe_2(SO_4)_3 + H_2O + O_2\uparrow$$

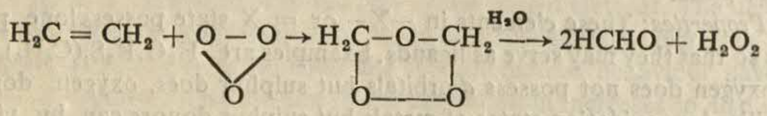
$$2HCl + O_3 \rightarrow Cl_2 + H_2O + O_2\uparrow$$

$$3SnCl_2 + 6HCl + O_3 \rightarrow 3SnCl_4 + 2H_2O$$

$$3SO_2 + O_3 \rightarrow 3SO_3$$

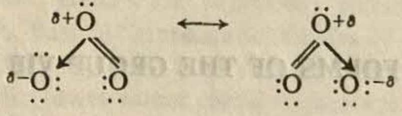
$$2KI + H_2O + O_3 \rightarrow I_2 + 2KOH + O_2\uparrow$$

$$H_2O_2 + O_3 \rightarrow H_2O + 2O_2\uparrow$$



$$H_2C = CH_2 + \underset{\diagdown\ O\ \diagup}{O - O} \rightarrow \underset{|\qquad\quad |}{H_2C-O-CH_2} \xrightarrow{H_2O} 2HCHO + H_2O_2$$

Ozone has a planar structure with O—O—O angle ~ 117° and O—O bond lengths intermediate between single bonds and double bonds. The oxygen—oxygen single bond and double bond lengths are 1.49A and 1.21A respectively while actual oxygen—oxygen bond length in ozone is 1.278A. Following resonating structures can be written (19-I):



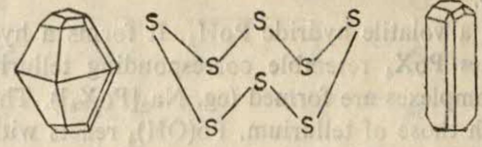
(19-I)

Each oxygen is sp^2 hybridised. The central oxygen has the following electron distribution in the hybridised orbitals:

$$\underset{2(sp^2)}{\underline{\uparrow\downarrow}}\quad \underset{2(sp^2)}{\underline{\uparrow\downarrow}}\quad \underset{2(sp^2)}{\underline{\uparrow}}\quad \underset{2p}{\underline{\uparrow}}$$

One sp^2 makes the lone pair and another the coordinate link. The third sp^2 with a proper overlap with the other oxygen orbital (with one unpaired electron) makes a sigma bond. The second electron in a $2p$ orbital then overlaps with another single electron of the other oxygen making the π-bond. The double bond is thus composed of a sigma and a pi bond.

Two crystalline modifications of sulphur are known. *Rhombic* sulphur is stable at room temperature and the *monoclinic* form persists above 96°C. Both the forms possess S_8 puckered rings (Fig. 19.1). Molecular weight determinations of sulphur in CS_2 support S_8 units. The packings of the S_8 rings in the crystal lattice of the rhombic and the monoclinic form are different. The transition from the rhombic to the monoclinic form being slow the rhombic form may be rapidly heated upto its melting point (112.8°C). The monoclinic form melts at 119°C. Just above the melting point liquid sulphur still maintains the S_8 units but around 160°C many of the properties of the liquid change abruptly. Sudden cooling of the liquid or dropping the liquid into water gives *plastic sulphur*. This variety of sulphur can be drawn into fibres. The fibres are made of helical chains of sulphur atoms. Plastic sulphur is insoluble in organic solvents and slowly returns to the crystalline rhombic form. Just above the boiling point sulphur still persists with the S_8 units but further increase in temperature leads to dissociation of S_8 units successively to S_6, S_4 and S_2. Note that oxygen is O_2 under all normal conditions. This is another example of the general rule that structures with multiple bonds are common with the first short period elements while the later period elements prefer structures with formal single bonds. Recall that nitrogen is $N \equiv N$ whereas phosphorus and arsenic are P_4 and As_4. Also note that carbon dioxide is monomeric $O = C = O$ whereas SiO_2 is polymeric with Si—O—Si bonds.



rhombic S_8 ring monoclinic

Fig. 19.1. Crystalline forms of sulphur

Selenium also has rhombic and monoclinic forms with Se_8 puckered rings. Both these forms are obtained on evaporation of CS_2 solution of selenium below 72°C. Both these forms are, however, unstable and slowly change to a gray, polymeric form containing infinite chains of selenium atom spiralling around a crystal axis.

Only one form of tellurium is known, and this is isomorphous with the gray form of selenium.

19.3. POLONIUM

The radioactivity of the mineral pitchbelende was found to be much greater than what was expected on the basis of its uranium content alone. The Curies undertook a laborious analytical investigation of the mineral and finally came out with the discovery of polonium in 1898. Polonium is a member of the uranium decay series. It is an alpha emitter with a half life of ~ 140 days, producing an isotope of lead. It is nowadays obtained in nuclear reactors by the irradiation of bismuth:

$$^{209}_{83}\text{Bi} + ^{1}_{0}n \rightarrow ^{210}_{84}\text{Po} + ^{0}_{-1}e$$

Polonium (B. P. 962°C) can be separated from bismuth (B.P. 1420°C) by fractional distillation. The properties of polonium are on the whole those expected from its position. It resembles tellurium to a large extent, although cationic properties predominate in polonium. Inert pair effect is marked in the element and the predominant valence is 4.

Polonium forms a volatile hydride PoH_2. It forms a hydroxide $Po(OH)_4$. The polonium halides PoX_4 resemble corresponding tellurium halides. With alkali halides halo-complexes are formed (eg. $Na_2[PoX_6]$). These halocomplexes are isomorphous with those of tellurium. $Po(OH)_4$ reacts with acetylacetone to form a non-electrolytic complex $[Po(acac)_4]$.

19.4. BINARY OXIDES

Binary oxides may be classified in three different ways: (1) from their acid-base behaviour in water, (2) from structural viewpoint and (3) from the view point of composition.

19.4.1. Classification of oxides based on acid base behaviour in water: When an oxide MO reacts with water to release protons we call it an acidic oxide. If it releases hydroxyl ion we term it a basic oxide:

$$2MO + H_2O \rightarrow 2MOH - \begin{cases} - \rightleftharpoons M^+ + OH^- \ \ldots \text{ basic oxide} \\ - \rightleftharpoons MO^- + H^+ \ \ldots \text{ acidic oxide} \end{cases}$$

When an oxide is capable of showing both these characteristics the oxide is termed amphoteric. Whether the intermediate MOH is acidic, basic or amphoteric will depend on which of the above equilibria becomes dominant. If the cation M^{n+} has a high polarising power (small size, large charge) it would strongly attract the oxide ion and thus will allow only the acidic dissociation (Chapter 8). Again if M^{n+} has a small polarising power the basic dissociation alone will occur. In order to have amphoteric properties the element must possess neither too much nor too low polarising power. The alkali and the alkaline earth ions are poor polarisers, and hence they form basic oxides. The group VB, VIV and VIIB elements (N, P, S, F, Cl, Br, etc) can bind the oxygen via covalent bonds resulting in acidic oxides. Amphoteric behaviour of the oxides is exemplified by the oxides of Al, Be, Zn, Ga, As, etc.

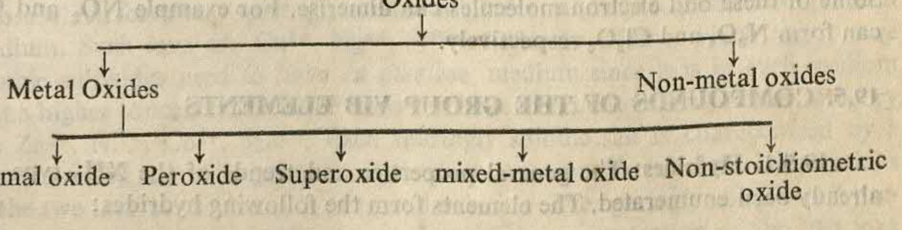
19.4.2. Structural Classification : From the structural standpoint the oxides may be classified as ionic, covalent and giant (or polymerised) covalent oxides. Although these three are extreme types, some oxides with intermediate properties also exist. In Table 19.3 we have included only the non-transition elements. Transition elements mostly form ionic or polymerised oxides. The structural classification of the oxides also points to the properties to be expected. For example, ionic oxides will be high melting, conducting in fused state and will have ionic crystal lattice. Covalent oxides will be composed of discrete, monomeric

Table 19.3. Classification of Oxides from Structural view point

	Ionic		*Polymerised*			*Small Covalent molecules*		
	Li	Be	B	C	N	O	F	
	Na	Mg	Al	Si	P	S	Cl	
	K	Ca	Ga	Ge	As	Se	Br	Kr
	Rb	Sr	In	Sn	Sb	Te	I	Xe
	Cs	Ba	Tl	Pb	Bi	Po	At	Rn
Oxide Formulas	M_2O							
	M_2O_2	MO	M_2O	MO	M_2O_3	MO_2	MO_2	
					MO_2	MO_3	M_2O_5	MO_3
	MO_2	MO_2	M_2O_3	MO_2	M_2O_5		MO_3	
							M_2O_7	

molecules with low boiling points, the force holding the molecules together in the crystal lattice being of the weak van der Waals type. However there are variations in the covalent group. CO_2 is monomeric but the oxides of phosphorus and arsenic though basically covalent, form tetrameric species P_4O_6 and As_4O_6. Silica has ionic-cum-covalent bonds but forms non-ending polymeric species. Note that the basic oxides and acidic oxides of the first classification correspond respectively to the ionic oxides and the covalent oxides of our second classification.

19.4.3. Classification based on composition



Normal Oxides: The formula of these oxides are decided on the basis of the oxidation number (−2) for divalent oxygen (eg: MgO, Na_2O, etc.).

Peroxides: These are salts of hydrogen peroxide (oxidation number of oxygen being −1) and have the peroxy links −O−O−. Peroxides of the alkalies and the alkaline earths and peroxysalts of S, C, P are well known.

Superoxides: These are formed by the larger alkalies and the alkaline earths. They are the final products of interaction of these metals with oxygen. The superoxide ion O_2^- has a uninegative oxidation state. On changing to the heavier alkali cations the stability of the peroxide and in particular, the superoxide increases relative to the normal oxide. For larger anions we need larger cations to counteract 'rattling' in the close packed type lattice (Chapters 6 and 14). Both peroxides and superoxides crystallise with large amounts of water due to strong hydrogen bonding. The alkali metal peroxides are among the strongest oxidants and often convert elements to their highest oxidation states.

Mixed metal oxides: On close packing of spheres (say of O^{2-} ions) two kinds of holes are created — octahedral and tetrahedral. Mixed metal oxides will arise when one metal ion occupies a particular hole and another metal ion occupies the other kind of holes. The type of holes filled depends on the size and the polarisability of the cation. *Spinels* have the general formula AB_2O_4 (A is a divalent ion and B as trivalent ion). In *magnesium ferrite* $MgFe_2O_4$ the iron (III) ions occupy the octahedral holes and the magnesium (II) ions the tetrahedral holes. In $MgAl_2O_4$ similar situation prevails. (p. 233; Part I)

Non-stoichiometric Oxides: The basic principle in the build-up of ionic crystal lattice is close packing of oxide ions and the occupation of the holes of the close packed system by metal ions of suitable size. FeO, for example, has a sodium chloride crystal structure but structure determination reveals that not all the iron atoms required by stoichiometry are present. Less than 50 atom % iron (II) are present, the formula being $Fe_{\sim 0.9}O$. In Fe_2O_3/Fe_3O_4 also the same oxide packing is present but many iron atoms are missing. In passing from FeO to Fe_2O_3 there is a gradual withdrawal of iron atoms. It is understandable that this removal will not be a clean process and the iron oxides have to be non-stoichiometric. Oxides of manganese and titanium also are non-stoichiometric.

Non-metal oxides: We have among the non-metal oxides purely covalent monomeric oxides such as CO_2, SO_2 etc. to polymeric SiO_2. Intermediate degree of polymerisation is also found. Molecular non-metal oxides are low boiling whereas the polymeric ones are high melting. Among the non-metal oxides there are a few odd electron molecules such as NO, NO_2, ClO_2, ClO_3, BrO_2 and BrO_3. Some of these odd electron molecules can dimerise. For example NO_2 and ClO_3 can form N_2O_4 and Cl_2O_6 respectively.

19.5. COMPOUNDS OF THE GROUP VIB ELEMENTS

19.5.1. Hydrides: The general properties and trends of the XH_2 type have already been enumerated. The elements form the following hydrides:

H_2O	H_2S	H_2Se	H_2Te	H_2Po
H_2O_2	H_2S_2			
	H_2S_3			
	H_2S_4			
	H_2S_6			

Of these hydrides H_2O alone is strongly hydrogen bonded. H_2O_2 is rather unstable, carries a peroxy $-O-O-$ linkage and behaves as a weak acid and, depending on surroundings, as an oxidant or as a reductant. Details of hydrogen peroxide and peroxysalts are given in **19.5.5.**

Hydrogen Sulphide: It is generally obtained in the laboratory by the action of non-oxidising acids such as HCl on ferrous sulphide:

$$FeS + 2HCl \rightarrow FeCl_2 + H_2S$$

Direct combination of the elements at elevated temperature also provides the hydrides. By cooling the reaction mixture to $\sim -60°C$ H_2S may be liquefied and then purified by distillation. A convenient laboratory method consists of heating a mixture of solid sulphur with paraffin (C_nH_{2n+2}, n being large). The chemistry of H_2S may be grouped under the following heads: (1) acid properties, (2) reducing properties, (3) precipitating properties and (4) polysulphide forming properties.

The gas is soluble in water to form $\sim 0.1M$ solution. This is a weak dibasic acid with $K_A^I \sim 10^{-7}$ and $K_A^{II} \sim 10^{-15}$:

$$H_2S \rightleftharpoons H^+ + HS^-; \; K_A^I = \frac{[H^+][HS^-]}{[H_2S]} = \sim 10^{-7}$$

$$HS^- \rightleftharpoons H^+ + S^{2-}; \; K_A^{II} = \frac{[H^+][S^{2-}]}{[HS^-]} = \sim 10^{-15}$$

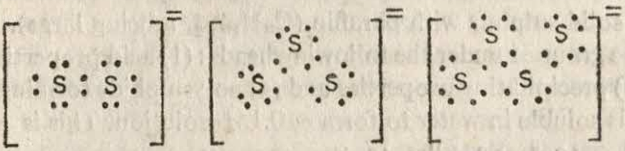
$$\text{Then} \qquad K_A^I \cdot K_A^{II} = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = \sim 10^{-22}$$

Water saturated with H_2S has $[H_2S] = 0.1\ M$. The concentrations of H^+, S^{2-} and H_2S will be regulated by the conditions prevailing in solution such that the product of K_A^I and K_A^{II} remain the same i.e. 10^{-22}. Thus addition of H^+ (acid) to a saturated solution appreciably lowers the $[S^{2-}]$ and the $[HS^-]$. Concentration of the H_2S molecules (undissociated form) is comparatively very high ($0.1M$) and therefore remains almost unaltered. Conversely the removal of H^+ ions (by the addition of alkali i.e. OH^- ions) appreciably increases the concentrations of both the HS^- and S^{2-} ions.

The insolubility of the metal sulphides varies to a good degree in solution. Those which form very sparingly soluble sulphides can be precipitated even in acid medium. Such ions are Cu^{2+}, Hg^{2+}, As^{3+}, Cd^{2+} etc. Metals which form more soluble sulphides need to have an alkaline medium since it is in such medium that a higher concentration of S^{2-} ions can be reached. Metal ions of this category are Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}. Each sparingly soluble salt is characterised by a product called solubility product (K_{SP}) which is the product of the concentrations of the two ions of the salt in a saturated solution. The sparingly soluble salt precipitates out of solution when the product of the concentration of the two ions in solution exceeds its K_{SP} value. A bivalent metal sulphide MS will be precipitated from solution when the concentration product ($[M^{2+}]\,[S^{2-}]$) exceeds its K_{SP}. The K_{SP} value of HgS is $\sim 10^{-52}$ whereas those for MnS, NiS, ZnS are $\sim 10^{-13}$, $\sim 10^{-22}$, $\sim 10^{-23}$. A separation of metal ions becomes possible by regulating the acidity of the solution prior to introducing H_2S for precipitating the metal sulphides.

Experiments show that the S^{2-} concentration in a saturated solution of H_2S in 0.3 *M* HCl is just high enough to precipitate insoluble sulphides like HgS ($K_{SP} \sim 10^{-52}$), CuS ($K_{SP} \sim 10^{-45}$) whereas it is too low to exceed the K_{SP} of more soluble sulphides like ZnS, NiS.

When sulphur is boiled with solution of alkali sulphide, polysulphides are formed. The resulting solutions are yellow to dark red. Depending on the concentration of the soluble sulphide and the amount of sulphur added, the composition of the polysulphide ions varies. Disulphide (S_2^{2-}), trisulphide (S_3^{2-}), tetrasulphide (S_4^{2-}) and pentasulphide (S_5^{2-}) are known. Some of these can be represented as in (19-II). The formation of the polysulphide ion is an exhibition of the basic reaction (Lewis donor) of the sulphide ion. Cautious distillation of an acidified polysulphide solution provides the free hydrides H_2S_2, H_2S_4, H_2S_3 etc. The polysulphides on standing after acidification ultimately lead to decomposition into S^{2-} ion and S.



(19-II)

In acid solution the standard potential of S/H_2S couple is + 0.14 volts.

$$S + 2H^+ + 2e \rightleftharpoons H_2S\ ;\ E^\circ = +0.14 \text{ volts}$$

Consequently H_2S can be readily oxidised to sulphur by a large number of oxidants:

$$5H_2S + 2KMnO_4 + 3H_2SO_4 \rightarrow 5S + 2MnSO_4 + K_2SO_4 + H_2O$$

$$3H_2S + K_2Cr_2O_7 + 4H_2SO_4 \rightarrow 3S + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

$$H_2S + 2HNO_3 \rightarrow S + 2NO_2 + 2H_2O$$

Hydrogen Selenide: This can be obtained by the hydrolysis of a metal selenide, say aluminium selenide, in water or a dilute non-oxidising acid:

$$Al_2Se_3 + 3H_2O \rightarrow 3H_2Se + Al_2O_3$$

The metal selenide is obtained by the interaction of the metal and selenium at elevated temperature. The hydride can also be obtained by heating finely powdered selenium with long chain hydrocarbon at 300—400°C. Selenium is often used in synthetic organic chemistry for the dehydrogenation of hydrocarbons via H_2Se.

H_2Se is more soluble in water than H_2S. Although a weak acid it is far stronger than H_2S (K_A^I for $H_2S \sim 10^{-7}$; K_A^I for $H_2Se \sim 10^{-4}$). Hydrogen selenide precipitates heavy metals such as silver and lead as metal selenides from solutions of their salts. This is a reducing agent, and is oxidised to selenium by oxidants such as oxygen, nitric acid, permanganate etc. Just as H_2S does with SO_2, H_2Se also reacts with SeO_2 to form Se:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O\ ;\ 2H_2Se + SeO_2 \rightarrow 3Se + 2H_2O$$

If H_2Se is treated with sulphur a substitution occurs with the formation of H_2S and Se, the reaction being analogous to that between halogens and halogen hydracids.

Hydrogen telluride: This is formed by the hydrolysis of aluminium telluride in water or in non-oxidising acid. Aluminium telluride Al_2Te_3 can be made by heating finely divided aluminium with tellurium.

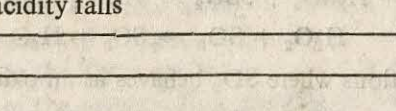
19.5.2. Oxides of Group VIB Elements : The important and well established oxides of this group are included in Table 19.4.

Table 19.4. Oxides of the Group VIB Elements

Oxidation Number	S	Se	Te	Po	acidity increases ↓
+1	S_2O				
+4	SO_2	SeO_2	TeO_2	PoO_2	
+6	SO_3	SeO_3	TeO_3		
	acidity falls →				

The lower oxide S_2O is produced when a glow discharge is passed through SO_2 It is very unstable decomposing to SO_2 and polymeric oxides.

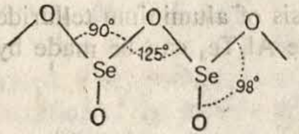
Dioxides: All the dioxides are made by burning the elements in air. Some metal sulphides, such as Cu_2S, also produce SO_2 on burning in air. On treatment with hot dilute nitric acid selenium and tellurium produce selenic acid H_2SeO_4 and $2TeO_2.HNO_3$ respectively. When these acid solutions are heated the dioxides are obtained. The two dioxides SO_2 and SeO_2 have very different properties. Whereas SO_2 is monomeric, covalent and gaseous, SeO_2 is polymeric, covalent and comparatively high melting (sublimes, 315°C). The structure of SO_2 can be represented by the resonating forms (19-III). Other possible forms can also be written (Chapter 5) but these will make smaller contribution to the resonance hybrid. The bond angle O—S—O is ~ 120° indicating sp^2 hybridisation of sulphur. The six outer orbital electrons of sulphur can be arranged in sp^2 hybridised state as:



(19-III)

$$S\ \underset{3s}{\underline{\uparrow\downarrow}}\ \underset{3p}{\underline{\uparrow\downarrow}}\ \underset{3p}{\underline{\uparrow}}\ \underset{3p}{\underline{\uparrow}}\ \xrightarrow{\text{hybridises to}}\ \underset{3(sp^2)}{\underline{\uparrow\downarrow}}\ \underset{3(sp^2)}{\underline{\uparrow\downarrow}}\ \underset{3(sp^2)}{\underline{\uparrow}}\ \underset{3p}{\underline{\uparrow}}$$

One sp^2 orbital carries the lone pair of electrons and another sp^2 orbital with paired electrons makes the coordinate bond to one oxygen. The electron in the third sp^2 orbital overlaps with an unpaired electron in the second oxygen orbital. The last electron in the $3p$ orbital of sulphur then overlaps with a suitable orbital of the second oxygen (having one spin) to form the π-bond. Thus the double bond is made up. Resonance is indicated by considerable double bond character of the S—O bonds. Selenium dioxide forms infinite covalently linked chain (19-IV). The bond angles show that the chain is non-planar. The structure breaks in the gas phase to the monomeric covalent form of SeO_2.



(19-IV)

Sulphur dioxide is a reducing agent as is shown by the following reactions:

$$2KMnO_4 + 5SO_2 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

$$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4$$

$$Cl_2 + SO_2 + 2H_2O \rightarrow 2HCl + H_2SO_4$$

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

$$H_2O_2 + SO_2 \rightarrow SO_3 + H_2O \rightarrow H_2SO_4$$

There are certain reactions where SO_2 behaves as an oxidant:

$$2H_2S + SO_2 \rightarrow 3S + H_2O$$

$$SO_2 + C \xrightarrow{1100^\circ C} CO_2 + S$$

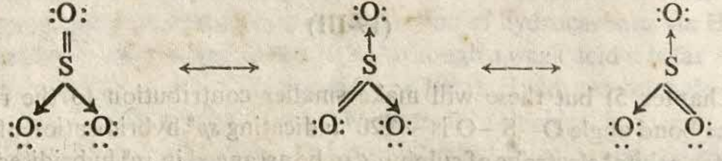
$$4FeCl_2 + SO_2 + 4HCl \longrightarrow 4FeCl_3 + 2H_2O + S$$

It has been studied as a non-aqueous solvent. Liquid SO_2 ionises as $2SO_2 \rightleftharpoons SO^{2+} + SO_3^{2-}$. By virtue of its lone pair it can function as a Lewis base.

Selenium dioxide, on the contrary, behaves as an oxidant particularly towards some organic compounds. SeO_2 is used in oxidising aldehydes and ketones:

$$R-CH_2-CO-R + SeO_2 \rightarrow R-CO-CO-R + Se + H_2O$$

Sulphur trioxide, being the anhydride of sulphuric acid, is of great industrial importance. It is obtained by the oxidation of SO_2 by oxygen in the presence of a catalyst (V_2O_5 or platinum sponge). In the gas phase it may be represented as a resonance hybrid of the following planar, triangular structures (19-V):



(19-V)

We again invoke sp^2 hybridisation: two electron pairs forming the two coordinate links; one unpaired electron in the third sp^2 hybrid overlaps with an electron in oxygen orbital and the second electron in the remaining *p*-orbital of sulphur forms a π-bond with oxygen:

$$\underbrace{\overset{\uparrow\downarrow}{\underline{3(sp^2)}}\quad\overset{\uparrow\downarrow}{\underline{3(sp^2)}}}_{\substack{\text{form coordinate}\\ \text{bonds with oxygen}}}\quad\underset{\substack{\text{forms}\\ \sigma\text{-bond}}}{\overset{\uparrow}{\underline{3(sp^2)}}}\quad\underset{\substack{\text{forms}\\ \pi\text{-bond}}}{\overset{\uparrow}{\underline{3p}}}$$

The extremely short S—O bond length (1.43A) points to additional π-bonding between filled oxygen *p*-orbitals and vacant sulphur *d*-orbitals.

At low temperature SO_3 stays as a polymeric solid $(SO_3)_3$ or as infinite helical chains. SO_3 is a powerful oxidant oxidising HBr to Br_2 and P to P_4O_{10}.

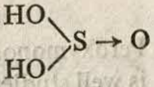
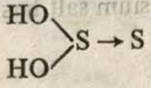
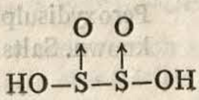
Selenium trioxide is formed alongwith much dioxide on passing electric discharge through a mixture of selenium vapour and oxygen under low pressure. It is the anhydride of selenic acid H_2SeO_4. Strong heating of telluric acid H_6TeO_6 gives TeO_3.

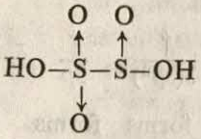
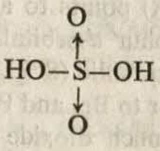
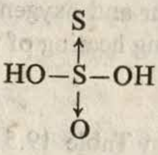
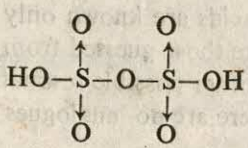
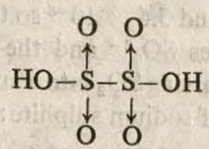
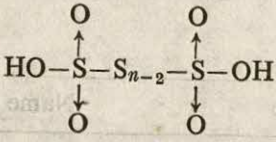
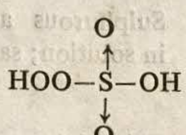
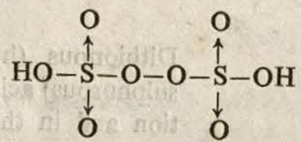
19.5.3. Oxyacids of Sulphur : We name in Table 19.5 only the important oxyacids of sulphur. Some of the oxyacids are known only in the form of salts and the structures given in the Table are those guessed from the salts. The structures shown are but one of the several other possible resonating forms. Oxyacids with S—S links are called thioacids. There are no analogues of thioacids in tellurium and selenium.

Sulphurous acid: This is formed when SO_2 is dissolved in water. The two acid dissociation constants are 1.7×10^{-2} and 5.6×10^{-8} so that it is not a strong acid. It forms two series of salts, sulphites SO_3^{2-} and the bisulphites HSO_3^-. *Sodium bisulphite* is commercially made by passing SO_2 into a suspension of sodium carbonate or through a saturated solution of sodium sulphite:

$Na_2CO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3 + CO_2$; $Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3$

Table 19.5. Oxyacids of Sulphur

Formula	Structure	Name and Comments
1. *Sulphurous Acid series*		
H_2SO_3		Sulphurous acid; known only in solution; salts are well known
$H_2S_2O_2$		Thiosulphurous acid
$H_2S_2O_4$	 $HO{-}\overset{\overset{O}{\uparrow}}{S}{-}\overset{\overset{O}{\uparrow}}{S}{-}OH$	Dithionous (hypo- or hydrosulphurous) acid; known in solution and in the form of salts; solutions are unstable.

Formula	Structure	Name and Comments
$H_2S_2O_5$	 $\mathrm{HO-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-\overset{\overset{O}{\uparrow}}{S}-OH}$	Pyrosulphurous acid; known only in the form of salts
2. Sulphuric Acid Series		
H_2SO_4	 $\mathrm{HO-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-OH}$	Sulphuric acid. Free acid and salts are well known
$H_2S_2O_3$	 $\mathrm{HO-\underset{\underset{O}{\downarrow}}{\overset{\overset{S}{\uparrow}}{S}}-OH}$	Thiosulphuric acid. Free acid is unstable. Salts are well known
$H_2S_2O_7$	 $\mathrm{HO-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-O-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-OH}$	Pyrosulphuric acid
3. Thionic Acid series		
$H_2S_2O_6$	 $\mathrm{HO-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-OH}$	Dithionic acid; known in aqueous solution and as salts.
$H_2S_nO_6$	 $\mathrm{HO-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-S_{\mathit{n}-2}-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-OH}$	Polythionic acid; known as salts. Free acids are not stable.
4. Peroxyacid series		
H_2SO_5	 $\mathrm{HOO-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-OH}$	Peroxymonosulphuric acid. Acid is well studied. An impure potassium salt has been reported.
$H_2S_2O_8$	 $\mathrm{HO-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-O-O-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-OH}$	Peroxydisulphuric acid. Acid is known. Salts are well known

The acid and its salts are reducing agents:

$$Cl_2 + H_2SO_3 + H_2O \rightarrow H_2SO_4 + 2HCl$$

$$2KMnO_4 + 5H_2SO_3 \rightarrow 2H_2SO_4 + 2MnSO_4 + K_2SO_4 + 3H_2O$$

$$K_2Cr_2O_7 + 3H_2SO_3 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O$$

In its reaction towards H_2S it may be viewed as an oxidant:

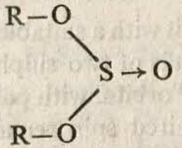
$$H_2SO_3 + 2H_2S \rightarrow 3S + 3H_2O$$

Sulphites react with sulphur to produce thiosulphates:

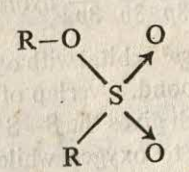
$$Na_2SO_3 + S \rightarrow Na_2S_2O_3$$

The valence shell of sulphur in the sulphite ion has $6 + 2 = 8$ electrons. Sulphur forms three coordinate links to the three oxygens and there is a lone pair. According to *VSEPR* theory the three bond pairs and the lone pair will be tetrahedrally disposed. Since there is a lone pair the overall shape will be pyramidal (cf: NH_3).

Organic sulphites R_2SO_3(R = alkyl group) have been shown to exist in two isomeric forms:



alkyl sulphite

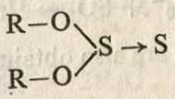


alkyl sulphonate

Thiosulphurous acid, $H_2S_2O_2$, is known only in the form of esters $R_2S_2O_2$ which are obtained by the reaction of sodium alkylate on S_2Cl_2 in non-aqueous solvent. These are monomers in benzene. These are easily hydrolysed by alkalies to give sulphur and thiosulphates. Two possible formulae are:

$$R-O-S-S-O-R$$

and



Dithionite (also called hydro- or hyposulphite) is formed on reduction of bisulphites with zinc:

$$2NaHSO_3 + Zn \rightarrow Na_2S_2O_4 + ZnO + H_2O$$

This is a very powerful reducing agent. It reduces cupric and mercuric salts to the respective metals and chromium (I) to chromium (0):

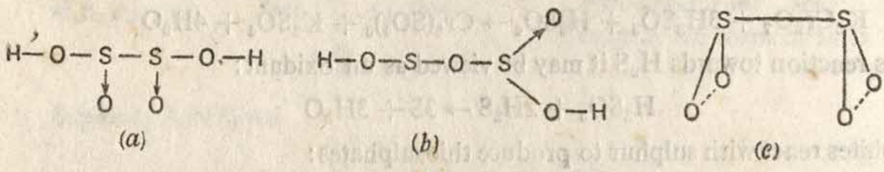
$$S_2O_4^{2-} + 4OH^- \rightarrow 2SO_3^{2-} + 2H_2O + 2e$$

$$CuCl_2 + Na_2S_2O_4 + 2H_2O \rightarrow Cu + Na_2SO_3 + H_2SO_3 + 2HCl$$

$$2[Cr(C_6H_6)_2]^+ + S_2O_4^{2-} + 4OH^- \rightarrow 2[Cr(C_6H_6)_2] + 2SO_3^{2-} + 2H_2O$$

For the last mentioned reaction see Chapter 26.

Dithionous acid was earlier thought to have a monomeric formula HSO_2 rather than $H_2S_2O_4$. This seemed to receive some support from the failure to obtain an acid salt. But diamagnetic behaviour of the salts ruled out the odd-electron HSO_2 formula and instead supported the dimeric even-electron $H_2S_2O_2$ formula. Two alternative structures (*a*) and (*b*) (19-VI) for the acid can be written:



(19-VI)

X-ray crystal structure of $Na_2S_2O_4$ supports structure (*a*) with very long S—S bond (2.39A) which is longer than that (~ 2A) in dithionate $^-O_3S-SO_3^-$. This long bond explains the unstable character and extreme reducing ability of dithionite. Dithionite solution is used to absorb molecular oxygen.

Each sulphur atom is sp^3 hybridised:

$$S \ \frac{\uparrow\downarrow}{3s}\ \frac{\uparrow\downarrow}{3p}\ \frac{\uparrow}{3p}\ \frac{\uparrow}{3p} \text{ hybridises to } \frac{\uparrow\downarrow}{3(sp^3)}\ \ \frac{\uparrow\downarrow}{3(sp^3)}\ \ \frac{\uparrow}{3(sp^3)}\ \ \frac{\uparrow}{3(sp^3)}$$

Overlap of one sp^3 orbital with one electron on it with a suitable *p* orbital of oxygen gives an S—O bond. Overlap of two sp^3 orbitals of two sulphur atoms with one electron on each gives the S—S bond. One sp^3 orbital with paired spins forms the coordinate link to oxygen while the other paired spin remains as a lone pair. Strong repulsion between the lone pairs results in the long S—S bond. $S_2O_4^{2-}$ has the structure shown in (*c*) with the oxygen atoms in eclipsed position ($< OSO = 108°$; $< SSO = 98°$).

Pyrosulphites are produced by the reaction of $NaHSO_3$ in solution with excess SO_2:

$$HSO_3^- + SO_2 \rightarrow HS_2O_5^- \xrightarrow{Na_2CO_3} Na_2S_2O_5$$

Pyrosulphites are also obtained by heating solid bisulphites:

$$2MHSO_3 \xrightarrow{\text{heat}} M_2S_2O_5 + H_2O$$

Pyrosulphites have an S—S link and an unsymmetrical structure, O_2S-SO_3.

Sulphuric Acid: It is a strong dibasic acid. The first step dissociation is complete in water and the second dissociation constant is ~ 10^{-2}. Most metals form sulphates and acid sulphates. The alkaline earth sulphates alone are very sparingly soluble in water.

Metal sulphates (and also selenates) can produce two kinds of double sulphates: (*a*) between a monovalent cation and a trivalent cation, called *alums,* $M^IM^{III}(XO_4)_2.12H_2O$ where M^I = Na, K, Rb, Cs, NH_4; M^{III} = Al, Cr, Fe, Mn, Co etc and X = S or Se; (*b*) between a monovalent cation and a bivalent cation, $M_2^IM^{III}(XO_4)_2.6H_2O$, called *schönites,* where M^I = univalent cation and M^{II} = bivalent cation. Heptahydrated bipositive metal sulphates are called *vitriols.*

Common examples are $CoSO_4.7H_2O$; $NiSO_4.7H_2O$; $FeSO_4.7H_2O$. Copper sulphate pentahydrate therefore is not a true vitriol.

Sulphuric acid is of great industrial importance. It is manufactured by two methods both involving catalytic oxidation of sulphur dioxide to sulphur trioxide. In the *contact process* a mixture of SO_2 and O_2 is passed over a catalyst (usually V_2O_5 or spongy platinum) at 450–500°C. When platinum catalyst is used the SO_2 gas must be very pure, particularly free from arsenic compounds in whose presence the platinum catalyst gets poisoned. The resulting SO_3 gas is not directly absorbed in water to produce H_2SO_4 since a fog of small droplets of H_2SO_4 is often formed. This fog dissolves in water only slowly. In practice SO_3 is absorbed into a dilute H_2SO_4 solution. The second commercial method is the *lead-chamber process* where the catalytic oxidation is carried out by nitrogen oxides in lead chambers. The oxides of nitrogen participate in the formation of some intermediate (nitrosyl sulphúric acid or nitrosyl bisulphate) which on treatment with water gives sulphuric acid and regenerates the nitrogen oxides.

$$2SO_2 + O_2 + H_2O + NO + NO_2 \rightarrow 2NO[HSO_4]$$
$$2NO[HSO_4] + H_2O \rightarrow 2H_2SO_4 + NO + NO_2$$

Solution of SO_3 in H_2SO_4 is called *oleum* or *fuming sulphuric acid*, which contains pyrosulphuric acid:

$$H_2SO_4 + SO_3 \rightarrow H_2S_2O_7$$

Sulphuric acid has a great affinity for water and form several crystalline hydrates: $H_2SO_4.H_2O$ (M.P. 8.5°C), $H_2SO_4.2H_2O$ (−39.5°C) and $H_2SO_4.4H_2O$ (−28°C). It serves as an excellent drying agent. Cellulose materials such as paper, cotton, wood, and sugar are charred by the acid:

$$C_{12}H_{22}O_{11} + 11H_2SO_4 \rightarrow 12C + 11H_2SO_4.H_2O$$

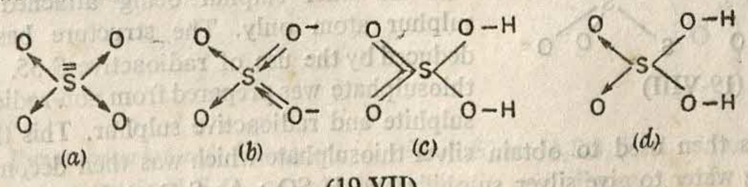
Metals above hydrogen in the electrochemical series (that is with positive standard electrode potential) do not dissolve in cold concentrated or dilute sulphuric acid, or in any other non-oxidising acid (Chapter 7). These metals, however, dissolve in hot sulphuric acid because the hot acid works as a good oxidant. Note that no hydrogen evolution occurs in these reactions:

$$2Ag + 2H_2SO_4 \rightarrow Ag_2SO_4 + SO_2 + 2H_2O$$
$$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$$

Carbon and sulphur are also oxidised:

$$C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$$
$$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$$

The sulphate ion is tetrahedral with sp^3 hybridised sulphur. Several structures can be written for the ion and the acid of which four are shown below (19-VII):


(a) (b) (c) (d)

(19-VII)

In structure (*a*) we assume sulphur to have a valence shell of $6 + 2 = 8$ electrons which are distributed in the four sp^3 orbitals. These orbitals make the coordinate links to the four oxygen. In structure (*b*) each of the two O^- ions have a valence shell of $6 + 1 = 7$ electrons. The sulphur has two pairs of electrons in the two sp^3 orbitals making the coordinate links. Two other hybrid orbitals overlap with oxygen *p*-orbitals to make one sigma bond each. The two O^- ions thus take their valence shells to $6 + 1 + 1 = 8$ electrons. Then a filled orbital of O^- overlaps with a vacant *d*-orbital of sulphur giving the double bond. The other structures are left as exercises. All four S—O distances are the same (1.44A) through resonance, and are considerably shorter than single bonds.

Sulphuric acid is widely used in the fertiliser industry to make ammonium sulphate and superphosphate. It is used to make esters, ethers, sulphates, other acids. Fuming sulphuric acid is used for sulphonation, that is, for introducing $-SO_3H$ group in organic compounds.

Thiosulphuric Acid: Boiling sulphur and an alkali sulphite produces sodium thiosulphate: $Na_2SO_3 + S \rightarrow Na_2S_2O_3$. This is better obtained by the interaction of alkali hydrogen sulphide and alkali bisulphite in solution:

$$2NaHS + 4NaHSO_3 \rightarrow 3Na_2S_2O_3 + 3H_2O$$

The sodium salt crystallises as a pentahydrate. This is a useful reducing agent:

$$Na_2S_2O_3 + Cl_2(\text{or } Br_2) + H_2O \rightarrow Na_2SO_4 + S + 2HCl\ (\text{or } HBr)$$

With iodine, thiosulphate is oxidised to tetrathionate, and this reaction serves as the basis of all iodometric estimations:

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

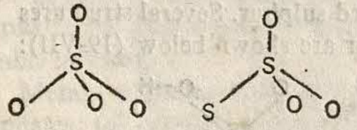
The reaction between $FeCl_3$ and excess $Na_2S_2O_3$ proceeds as under:

$$2Na_2S_2O_3 + FeCl_3 \rightarrow Na[Fe(S_2O_3)_2] + 3NaCl$$
$$Na[Fe(S_2O_3)_2] + FeCl_3 + NaCl \rightarrow Na_2S_4O_6 + 2FeCl_2$$

Potassium permanganate gives sulphate in neutral solution but dithionate is also obtained in acid medium:

$$Na_2S_2O_3 + 2KMnO_4 \rightarrow Na_2SO_4 + K_2SO_4 + Mn_2O_3$$
$$5Na_2S_2O_3 + 6KMnO_4 + 9H_2SO_4 \rightarrow 5Na_2S_2O_6 + 3K_2SO_4 + 6MnSO_4 + 9H_2O$$

Sodium thiosulphate is used in photography as a fixing agent dissolving out the unreacted silver bromide as complexes $[Ag(S_2O_3)]^-$ and $[Ag(S_2O_3)_2]^{3-}$. The thiosulphate ion is structurally analogous to sulphate ion, one oxygen of the latter being replaced by a sulphur atom (19-VIII). Such a structure demands that the two sulphur atoms are non-equivalent: one sulphur being attached to three oxygen and one sulphur, and the other sulphur being attached to a sulphur atom only. The structure has been deduced by the use of radioactive S-35. Active thiosulphate was prepared from non-radioactive sulphite and radioactive sulphur. This thiosulphate was then used to obtain silver thiosulphate which was then decomposed by boiling water to give silver sulphide and H_2SO_4: $Ag_2S_2O_3 + H_2O \rightarrow Ag_2S +$



(19-VIII)

H_2SO_4. Interestingly the entire radioactivity appeared with the silver sulphide. If the two sulphur atoms were equivalent in the thiosulphate the radioactivity would not have appeared in the silver sulphide only. On boiling a solution of active sodium thiosulphate with acid a precipitate of active sulphur appears but no radioactivity is found in the SO_3^{2-} solution:

$$^{35}S + {}^{32}SO_3^{2-} \xrightarrow{\text{boil}} {}^{35}S^{32}SO_3^{2-} \xrightarrow{\text{acid}} {}^{35}S + {}^{32}SO_3^{2-}$$

This reaction shows that there is no exchange between the two S atoms, and hence they cannot be equivalent.

That the free acid may have the two structures: (*a*) with one OH and another SH group and (*b*) two OH groups (c.f. 19-VII) is indicated by the following reactions: hydrolysis of silver thiosulphate produces silver sulphide and sulphuric acid while that of thiosulphuric acid gives sulphur and sulphurous acid. Sodium thiosulphate reacts with C_2H_5 Br to give ethyl derivative of the acid:

$$NaO.SO_2.SNa + C_2H_5Br \rightarrow NaO.SO_2.SC_2H_5 + NaBr$$

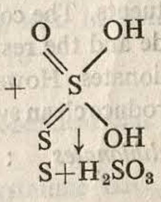
The ethyl derivative, on hydrolysis, produces ethyl mercaptan:

$$NaO.SO_2.SC_2H_5 + H_2O \rightarrow NaO.SO_2.OH + C_2H_5SH$$

This reaction shows that there is an —SH group in thiosulphuric acid.

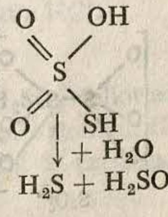
Ambidentate nature of thiosulphuric acid: Thiosulphate group may be attached to a metal ion either through an oxygen atom or through a sulphur atom. Air oxidation of a mixture of cobalt chloride, ammonium chloride, ammonia and sodium thiosulphate leads to the isolation of $[Co(S_2O_3)(NH_3)_5]Cl$ as purple crystals. This compound reacts with KCN, with evolution of ammonia, to give golden crystals of $K_4[Co(S_2O_3)(CN)_5]$. The silver salt $Ag_4[Co(S_2O_3)(CN)_5]$ could be carefully manipulated with HCl to give the free acid in two isomeric forms. The O-bonded form decomposes to give sulphur and H_2SO_3 while the S-bonded form produces H_2S and H_2SO_4:

(*a*) $H_4[Co(OS_2O_2)(CN)_5] + H_2O \rightarrow H_2[Co(H_2O)(CN)_5] +$



yellow

(*b*) $H_4[Co(SSO_3)(CN)_5] + H_2O \rightarrow H_2[Co(H_2O)(CN)_5] +$



red

Pyrosulphuric acid: When SO_3 is dissolved in H_2SO_4 in 1 : 1 proportion the major product is $H_2S_2O_7$ called pyrosulphuric acid. Pyrosulphuric acid behaves as a weak acid. Pyrosulphate salts are obtained by careful heating of bisulphate salts:

$$2MHSO_4 \underset{}{\overset{\sim 150°C}{\rightleftharpoons}} M_2S_2O_7 + H_2O$$

Strong heating of pyrosulphates leads to expulsion of SO_3 leaving behind the sulphates. $S_2O_7^{2-}$ is composed of $^-O_3S-O-SO_3^-$, the sulphur atoms being tetrahedral.

Dithionic Acid: Dithionic acid should not be considered as a member of the polythionic acid. As (19-IX b, c) show that in all polythionates there are one or more sulphur atoms which are linked only to sulphur atoms but not to any oxygen atom. On the contrary in dithionates both sulphur atoms are equivalent and both are connected to three oxygen and one sulphur atom (19-IX, a).

Dithionate is produced by the oxidation of sulphurous acid with MnO_2:

$$MnO_2 + 2SO_3^{2-} + 4H^+ \rightarrow Mn^{2+} + S_2O_6^{2-} + 2H_2O$$

Other less soluble sulphur-containing anions are precipitated by baryta, and the filtrate on concentration gives crystals of barium dithionate dihydrate. Only strong oxidants will oxidise dithionate to sulphate. The dithionate ion is made up of two tetrahedral units O_3S-SO_3. As in other sulphur oxyacids, here too, considerable double bond character of S–O bond (1.43A) is present.

Polythionic Acids: Mixtures of polythionates are obtained by (1) interaction of thiosulphate solutions with SO_2 in presence of arsenic (III) or by (2) the action of H_2S on aqueous solution of SO_2 (Wackenroder's solution): Wackenroder's

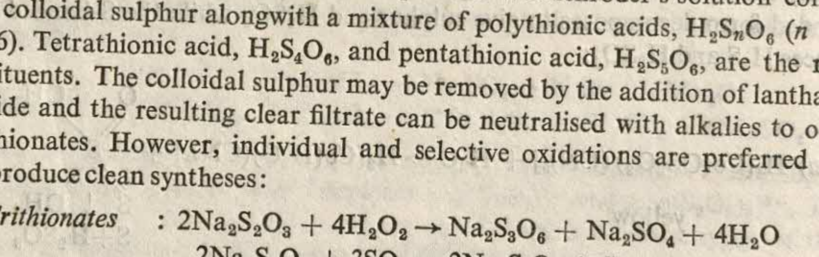
$$2Na_2S_2O_3 + 3SO_2 \rightarrow 2Na_2S_3O_6 + S$$

$$H_2S + 2SO_2 \rightarrow 3SO + H_2O;\ 5SO + H_2O \rightarrow H_2S_5O_6$$

solution is prepared by passing H_2S through SO_2-saturated water maintained at 0°C till the solution takes no more H_2S. This Wackenroder's solution contains some colloidal sulphur alongwith a mixture of polythionic acids, $H_2S_nO_6$ (n = 3, 4, 5, 6). Tetrathionic acid, $H_2S_4O_6$, and pentathionic acid, $H_2S_5O_6$, are the major constituents. The colloidal sulphur may be removed by the addition of lanthanum chloride and the resulting clear filtrate can be neutralised with alkalies to obtain polythionates. However, individual and selective oxidations are preferred since they produce clean syntheses:

Trithionates : $2Na_2S_2O_3 + 4H_2O_2 \rightarrow Na_2S_3O_6 + Na_2SO_4 + 4H_2O$

$$2Na_2S_2O_2 + 3SO_2 \rightarrow 2Na_2S_3O_6 + S$$



(a) (b) (c)

(19-IX)

Tetrathionates : $2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$

Pentathionates : $5Na_2S_2O_3 + 6HCl \xrightarrow[-10°C]{As(III)} 2Na_2S_5O_6 + 6NaCl + 3H_2O$

Hexathionate: The potassium salt can be obtained by the action of KNO_2 on $K_2S_2O_3$ in concentrated HCl solution at ~ 15°C. It separates as white crystals.

X-ray studies show the dithionate and the polythionates to have the structures (19-IX) indicating that the additional sulphur atoms make a zig-zag chain.

19.5.4. Oxyacids of Selenium and Tellurium : *Selenous acid:* This is formed when SeO_2 is dissolved in water. It gives two series of salts, the selenites SeO_3^{2-}, and the biselenites $HSeO_3^-$. Selenous acid and its salts are, unlike the sulphites, oxidants. Thus SO_2, HI and H_2S are oxidised to SO_3, I_2 and S respectively, with reduction of selenous acid or selenites to selenium.

Selenic Acid: This is obtained from selenous acid by refluxing with 30% H_2O_2. Fusion of selenium with KNO_3 gives potassium selenate. The free acid forms colourless crystals (M.P. 59°C). It is as strong an acid as H_2SO_4, and forms stable hydrates. Its salts are isomorphous with sulphates. The selenate ion is tetrahedral.

It forms alums, schönites and vitriols. Selenic acid is less stable than sulphuric acid. Thus selenic acid oxidises HI and HBr to the corresponding halogens more readily than does sulphuric acid. Zinc dust, SO_2 or N_2H_4 readily reduces dilute selenic acid to elementary selenium.

Tellurites: TeO_2 is practically insoluble in water but in alkalies gives tellurites and bitellurites.

Telluric Acid: This is quite different from H_2SO_4 and H_2SeO_4. The formula of telluric acid is H_6TeO_6 ($Te(OH)_6$). The difference is due to the relatively bigger size of tellurium so that it is possible to pack more oxygen or OH^- ions around it. This also holds true for the halogen family. Whereas perchlorate is ClO_4^-, the periodate is usually H_5IO_6. Telluric acid and its salts are obtained by the oxidation of TeO_2 by H_2O_2, Na_2O_2, CrO_3 etc. In contrast to the strong acid behaviour of H_2SO_4 and H_2SeO_4, telluric acid is a weak dibasic acid ($K_A^I \sim 10^{-7}$).

19.5.5. Hydrogen Peroxide : This important inorganic chemical can be obtained by the following methods:

1. *Acid treatment of a metal peroxide:* Colourless, crystalline $BaO_2.8H_2O$ can be decomposed by treatment with H_2SO_4 in presence of little HCl:

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$$

2. *Electrolytic Preparation:* Anodic oxidation of 50% H_2SO_4 followed by careful vacuum distillation constitutes an important method of obtaining H_2O_2. Peroxydisulphuric acid is first formed which is hydrolysed first to permonosulphuric acid and then to H_2O_2.

at the anode: $H_2SO_4 \rightarrow H^+ + HSO^-_4$; $2HSO^-_4 \rightarrow H_2S_2O_8 + 2e$

at the cathode: $2H^+ + 2e \rightarrow H_2$

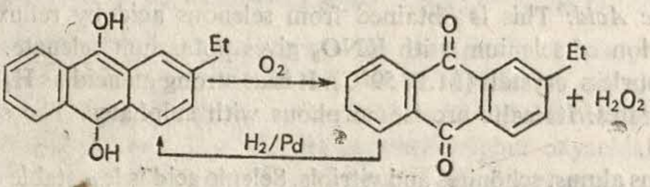
Hydrolysis:

$$\begin{aligned} H_2S_2O_8 + H_2O \rightarrow H_2SO_5 &+ H_2SO_4 \\ \downarrow & H_2O \\ H_2O_2 &+ H_2SO_4 \end{aligned}$$

Note that during the above oxidation process hydrogen alone is evolved at the cathode but no oxygen at the anode. Simultaneously with this reaction evolution of hydrogen and oxygen in the ratio of 2 vol: 1 vol occurs due to electrolysis of H_2O. So the overall result of electrolysis of moderately conc. H_2SO_4 is less of oxygen and more of hydrogen than one expects from water alone.

Alternatively K_2SO_4 and H_2SO_4 in 1 : 1 ratio may be mixed to produce $KHSO_4$ and then oxidised anodically to precipitate sparingly soluble potassium peroxydisulphate, $K_2S_2O_8$. This gives H_2O_2 on distillation with H_2SO_4 under low pressure.

3. *Synthesis via anthrahydroquinol:* 2-Ethyl anthrahydroquinol as 10% solution in a mixed solvent of benzene and higher alcohols is oxidised by oxygen



(19-X)

to 2-ethyl anthraquinone with simultaneous reduction of oxygen to H_2O_2. The hydrogen peroxide is extracted into an aqueous layer and concentrated by vacuum distillation. The anthraquinone can be reduced by hydrogen with a palladium catalyst to the anthrahydroquinol and reused (19-X).

Aqueous solution of H_2O_2 can be carefully distilled under reduced pressure. At first water distills over since H_2O_2 has a higher boiling point. The later fractions are collected and reduced pressure distillation repeated to get almost 99% H_2O_2. On cooling to ~ − 10°C crystals of H_2O_2 (M.P. −0.89°C) can be obtained. Commercially only aqueous solutions are marketed. The strength of H_2O_2 is stated in terms of the volume of oxygen evolved on heating ($H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$). Thus 10 vol. H_2O_2 means the H_2O_2 solution can give off on heating 10 times its volume of oxygen. Since 34 gm. H_2O_2 can give ($\frac{1}{2} \times 22.4$) litres of oxygen at N. T. P. then each gram of H_2O_2 will give 329.4 ml of oxygen. Therefore 1% H_2O_2 solution liberates 3.294 times its own volume of oxygen; 10 vol. H_2O_2 has a strength of 3.04% H_2O_2. The 100 vol. or ~ 30% H_2O_2 is called *perhydrol*. Hydrogen peroxide solutions are stabilised by little H_2SO_4, H_3PO_4, alcohol or glycerol.

Reactions of Hydrogen Peroxide: In its chemical reactions H_2O_2 can function as an acid, as an oxidant and as a reductant.

1. *Acid Behaviour:* It behaves as a weak dibasic acid:

$$H_2O_2 \rightleftharpoons H^+ + HO_2^-; \; K_A^1 \sim 1.5 \times 10^{-12}$$

It is thus slightly more acidic than water. The second dissociation is very weak. It gives two series of salts: normal peroxides, Na_2O_2, BaO_2 etc and the hydroperoxide $NaHO_2$. When Na_2O_2 is added to ethyl alcohol containing a little sodium ethoxide the following reaction occurs:

$$Na_2O_2 + EtOH \rightarrow NaOOH + NaOEt$$

In the absence of the ethoxide, the hydroperoxide formed reacts with ethanol to form sodium ethoxide and H_2O_2. Alkali metal peroxides are celebrated oxidants. The hydroperoxide is a violent oxidant unless carefully handled. It has been used to oxidise cupric oxide to copper sesquioxide Cu_2O_3 in concentrated NaOH medium.

2. *Oxidising Behaviour:* This is a strong oxidant in both acid and alkaline solution. The redox potentials are:

$$H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O \;; \qquad E^\circ = 1.77 \text{ volts}$$
$$HO_2^- + H_2O + 2e \rightleftharpoons 3OH^- \;; \qquad E^\circ = 0.87 \text{ volts}$$

The oxygen-oxygen bond of H_2O_2 undergoes fission in presence of H^+ and electrons acquired from the reducing agents. H_2O_2 is thus converted to H_2O. The high positive potential shows that in acid solution it can easily oxidise iron (II) to iron (III) ($E^\circ = 0.77$ volts), bromide to bromine ($E^\circ = 1.07$), iodide to iodine ($E^\circ = 0.54$) etc:

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$$
$$2I^- + H_2O_2 + 2H^+ \rightarrow I_2 + 2H_2O$$

Discoloured oil paintings in which the white lead pigment (basic lead carbonate) has been blackened due to atmospheric H_2S can be restored by scrubbing with H_2O_2:

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$$

Arsenious acid and sulphurous acids are oxidised to arsenic and sulphuric acid respectively:

$$H_3AsO_3 + H_2O_2 \rightarrow H_3AsO_4 + H_2O$$
$$H_2SO_3 + H_2O_2 \rightarrow H_2SO_4 + H_2O$$

3. *Reducing Behaviour:* In presence of some very strong oxidants such as chlorine or permanganate in acid medium H_2O_2 is oxidised to oxygen. In another word H_2O_2 acts as a reducing agent. In the oxidising reactions of H_2O_2 it is reduced to H_2O while in the reducing reactions H_2O_2 is oxidised to O_2: The hydrogen-oxygen bonds of H_2O_2 undergo fission to produce $2H^+$, $2e$ and O_2. The released electrons bring about the reduction.

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$$
$$Cl_2 + H_2O_2 \rightarrow 2HCl + O_2$$

Hydrogen peroxide oxidises ferrocyanide to ferricyanide in acid medium but reduces ferricyanide to ferrocyanide in alkaline medium:

$$2[Fe(CN)_6]^{4-} + H_2O_2 + 2H^+ \rightarrow 2[Fe(CN)_6]^{3-} + 2H_2O$$
$$2[Fe(CN)_6]^{3-} + H_2O_2 + 2OH^- \rightarrow 2[Fe(CN)_6]^{4-} + 2H_2O + O_2$$

Experiments with O-18 labelled H_2O_2 has shown that the oxygen that is liberated during reducing activities of H_2O_2 originates from H_2O_2 and not from H_2O of the aqueous medium. This points out that the oxidants do not break the O—O link of H_2O_2.

Hydrogen peroxide has an interesting *skew* structure. The two O—H planes are approximately perpendicular to each other (Fig. 19.2). Recall that oxygen has the following outer electronic configuration:

$$\underset{2s}{\underline{\uparrow\downarrow}}\ \underset{2p}{\underline{\uparrow\downarrow}}\ \underset{2p}{\underline{\uparrow}}\ \underset{2p}{\underline{\uparrow}}$$

Taking the x axis as the bond axis of O—O linkage the $2p_x$ orbitals of the two oxygen atoms overlap to give a sigma bond. Each oxygen also makes a sigma bond with a hydrogen, one oxygen using its $2p_y$ orbital and the other oxygen using its $2p_z$ orbital for the purpose. Then the two oxygen have their third $2p$ orbital carrying the lone pairs at right angles and directed away from each other. Thus the lone pair—lone pair repulsion can be minimised.

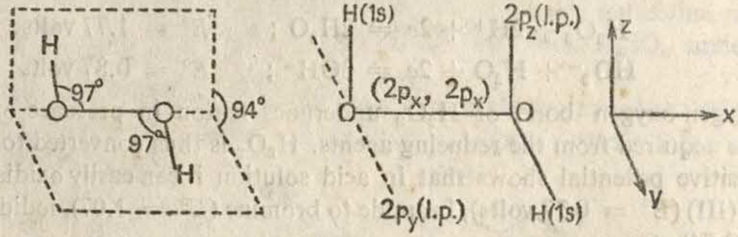


Fig. 19.2. Structure of H_2O_2 : l.p. = lone pair

19.5.6. Metal Peroxides: Metal peroxides are normal salts of H_2O_2 and contain the O_2^{2-} anion. The anion being quite large is not stabilised by small cations like Li^+ (Chapter 14). Sodium and the other alkalies as also Ca, Sr and Ba form peroxides. All peroxides are highly hydrated eg: $Na_2O_2.8H_2O$; $CaO_2.8H_2O$ due to hydrogen bonding. Air oxidation of sodium first produces Na_2O which is oxidised further to Na_2O_2. Crystallisation from ice-water gives the octahydrate. Barium peroxide is made by the action of air or oxygen on barium monoxide at 500°C.

All peroxides are stong oxidants. Fusion of chromium (III) and manganese (II) salts with Na_2O_2 gives yellow chromates and green manganates respectively. Finely divided iron reacts violently to give ferrates Na_2FeO_4.

19.5.7. Peroxyacids and Peroxysalts: There are some oxyacids which also contain peroxy linkage. These are called peroxyacids and their salts called peroxysalts. Sulphur, phosphorus, carbon, and boron form well defined peroxyacids and peroxysalts.

1. *Peroxysulphuric acids and peroxysulphates:* Potassium peroxydisulphate is obtained by the anodic oxidation of potassium bisulphate or a 1 : 1 mixture of K_2SO_4 and H_2SO_4. The bisulphate solution is taken in wide glass test tube into which is lowered an open tube. A copper spiral is wound around this open

tube which serves as the diaphragm. Inside the open tube there is a thick platinum wire hanging, which serves as the anode. The copper spiral serves as the cathode. Electrolysis is carried out with a high current density and at low temperature (ice bath). Soon sparingly soluble crystals of $K_2S_2O_8$ separate out:

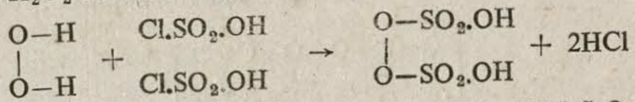
$$KHSO_4 \rightarrow K^+ + HSO_4^-$$

$$\textit{at the anode}: 2HSO_4^- \rightarrow H_2S_2O_8 + 2e$$

$$H_2S_2O_8 \rightarrow 2H^+ + S_2O_8^{2-};\ 2K^+ + S_2O_8^{2-} \rightarrow K_2S_2O_8$$

$$\textit{at the cathode}: 2H^+ + 2e \rightarrow H_2$$

Electrolysis of 50% H_2SO_4 at 0°C with a Pt anode and a high current density gives peroxydisulphuric acid $H_2S_2O_8$. The peroxyacid can also be obtained by the action of pure H_2O_2 on chlorosulphuric acid (also called chlorosulphonic acid):



$$\begin{matrix} O-H \\ | \\ O-H \end{matrix} + \begin{matrix} Cl.SO_2.OH \\ \\ Cl.SO_2.OH \end{matrix} \rightarrow \begin{matrix} O-SO_2.OH \\ | \\ O-SO_2.OH \end{matrix} + 2HCl$$

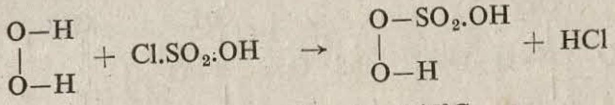
On removing the HCl under vacuum colourless crystals of $H_2S_2O_8$ (*Marshall's acid*) (M.P. 65°C) are obtained. Peroxymonosulphuric acid, H_2SO_5 (*Caro's acid*), is obtained on hydrolysis of $H_2S_2O_8$:

$$H_2S_2O_8 + H_2O \rightarrow H_2SO_4 + H_2SO_5$$

The acid is obtained also on treating anhydrous SO_3 with 100% H_2O_2:

$$H_2O_2 + SO_3 \rightarrow H_2SO_5$$

This can also be prepared by the reaction of chlorosulphonic acid and H_2O_2 in 1 : 1 ratio:



$$\begin{matrix} O-H \\ | \\ O-H \end{matrix} + Cl.SO_2.OH \rightarrow \begin{matrix} O-SO_2.OH \\ | \\ O-H \end{matrix} + HCl$$

Permonosulphuric acid is crystalline and melts at 45°C.

The peroxysulphates are among the most important and useful oxidants. The ammonium, sodium and potassium peroxydisulphates are commercially available materials. The standard potential of $S_2O_8^{2-} + 2e \rightleftharpoons 2SO_4^{2-}$ is + 2.01 volts, and thus peroxydisulphate can oxidise ferrous to ferric, manganese (II) to permanganate (in presence of Ag^+) etc. Peroxidisulphates are used in the syntheses of higher oxidation states, namely, silver (II), silver (III), manganese (IV), copper (III) etc:

$$2FeSO_4 + K_2S_2O_8 \rightarrow Fe_2(SO_4)_3 + K_2SO_4$$

$$2MnSO_4 + 5K_2S_2O_8 + 8H_2O \rightarrow 2KMnO_4 + 4K_2SO_4 + 8H_2SO_4$$

$$2KI + K_2S_2O_8 \rightarrow I_2 + 2K_2SO_4$$

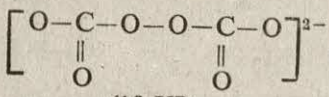
$$K_2S_2O_8 + 2AgNO_3 + 2H_2O \rightarrow 2AgO + 2KHSO_4 + 2HNO_3$$

$$Mn(OH)_2 + K_2S_2O_8 \rightarrow MnO_2 + 2KHSO_4$$

Peroxyacids or peroxysalts give H_2O_2 on treatment with dilute H_2SO_4. Peroxyacids and peroxysalts are generally tested by the Riesenfild reaction, that is, by the addition of a solution of the acid or salt to a 30% KI buffered to pH 7-8 with sodium bicarbonate when iodine is liberated. Decolourisation of acid permanganate is also another suitable test for peroxyacids and their salts.

In this context it is pertinent to mention that there is still an unfortunate practice of calling peroxyacids and peroxysalts simply as peracids and persalts. This unhealthy practice should be dropped since 'per' merely indicates a higher oxidation number of the central element such as in perchlorate or permanganate. These latter compounds have no peroxy linkage and will not decolourise acidic permanganate. Unequivocal proof of the presence of a peroxy linkage in a peroxysalt, however, has to come from crystal structure studies.

2. *Peroxycarbonate*, $K_2C_2O_6$: This is obtained as a pale blue crystalline material by anodic oxidation of a concentrated aqueous solution of K_2CO_3 at $\sim -15°C$ with a high current density at a platinum anode. The compound liberates iodine from iodide ion, oxidises lead sulphide to sulphate. It has structure (19-XI):



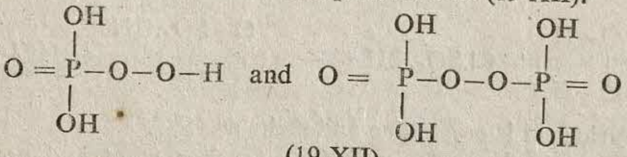
$$\left[\mathrm{O{-}\underset{\underset{O}{\|}}{C}{-}O{-}O{-}\underset{\underset{O}{\|}}{C}{-}O}\right]^{2-}$$

(19-XI)

3. *Peroxydiphosphate*, $K_4P_2O_8$: It has been obtained by the anodic oxidation of potassium hydrogen phosphate in presence of KF. In strongly acid solution hydrolysis occurs first to peroxymonophosphoric acid and finally to H_2O_2:

$$K_4P_2O_8 \xrightarrow{H_2O} H_3PO_5 \xrightarrow{H_2O} H_3PO_4 + H_2O_2$$

The two peroxyphosphoric acids can be represented as (19-XII).



$$\mathrm{O{=}\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{P}}{-}O{-}O{-}H} \quad \text{and} \quad \mathrm{O{=}\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{P}}{-}O{-}O{-}\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{P}}{=}O}$$

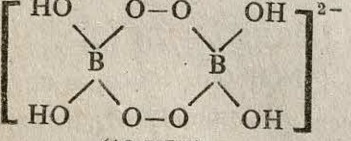
(19-XII)

4. *Peroxyborates:* Peroxyborates of sodium and potassium are generally precipitated by the addition of alcohol to a solution containing a metaborate and H_2O_2. The sodium salt has also been prepared by the action of boric acid on sodium hydroperoxide.

$$KBO_2 + H_2O_2 \rightarrow KBO_3 + H_2O; \; H_3BO_3 + NaOOH \rightarrow NaBO_3 + 2H_2O$$

These products are extensively hydrated, for example, $NaBO_3.4H_2O$. These are used in washing powders since in their aqueous solution H_2O_2 is released. Crystal structure determination has shown that some of the H_2O molecules participate in the constitution of the compound. These are binuclear peroxybridged compounds of the type:

$$2NaBO_3.4H_2O = Na_2[B_2O_6.2H_2O].6H_2O$$
$$= Na_2[B_2(O_2)_2(OH)_4].6H_2O.$$



(19-XIII)

The structure is (19-XIII) with two peroxy groups bridging two tetrahedral boron atoms.

5. *Transition Metal Peroxycompounds:* Peroxy compounds are well known with chromium, vanadium and titanium. In these compounds each peroxy group assumes two coordination positions around the transition metal. A three-membered strained ring will be formed at the metal atom. The peroxy compounds of vanadium and titanium form the basis of colorimetric estimation of the elements. For details see Chapters 24, 25 and 26.

19.5.8. Halides and Oxyhalides of Sulphur : *Sulphur Hexafluoride:* This is made by the combination of the elements: $S + 3F_2 \rightarrow SF_6$. This is a colourless, odourless and extremely inert gas. It refuses to react with fused KOH, steam at 500°C and oxygen in an electric discharge. Hexacovalence of sulphur is brought about by fluorine which is the smallest and the most electronegative of the halogens. Because of its inertness and insulation properties the gas is sometimes used as a gaseous insulator in high voltage generators and electrical instruments. Sulphur is octahedral through sp^2d^2 hybridisation. Since in SF_6 sulphur has already attained its maximum coordination number six it cannot accommodate any water molecule for nucleophilic attack which could lead to hydrolysis. The compound suffers no dissociation to $SF_4 + F_2$ in which case the SF_4 could be hydrolysed.

Sulphur tetrafluoride, SF_4, is best prepared by the action of SCl_2 and NaF in acetonitrile at around 70-80°C. As indicated above, SF_4 is highly reactive and suffers nucleophilic attack by H_2O to produce SO_2 and HF: $SF_4 + 2H_2O \rightarrow SO_2 + 4HF$.

Sulphur monochloride (in reality a dimer S_2Cl_2) is prepared as an orange liquid by the action of chlorine on fused sulphur. It is also formed as a by-product in the synthesis of CCl_4 from CS_2:

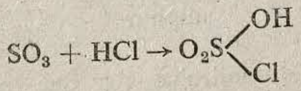
$$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$$

S_2Cl_2 (B.P. 138°C) can be separated from CCl_4 (B.P. 75°C) via fractional distillation. It is slowly hydrolysed by water:

$$S_2Cl_2 + 2H_2O \rightarrow SO_2 + 2HCl + H_2S$$

Its structure is comparable to that of H_2O_2.

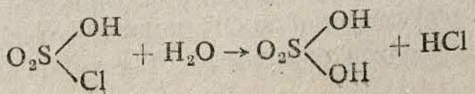
Chlorosulphonic (*chlorosulphuric*) *Acid* (HSO_3Cl): This may be viewed to be derived from sulphuric acid by substitution of one $-OH$ group by a chloro-group. It is prepared by passing HCl gas into fuming H_2SO_4.



$$SO_3 + HCl \rightarrow O_2S\Big\langle\begin{matrix}OH\\Cl\end{matrix}$$

Chlorosulphuric acid (B.P. 151°C) is purified by distillation.

It is violently hydrolysed by water giving HCl and H_2SO_4:



$$O_2S\Big\langle\begin{matrix}OH\\Cl\end{matrix} + H_2O \rightarrow O_2S\Big\langle\begin{matrix}OH\\OH\end{matrix} + HCl$$

It is used as a sulphonating agent in organic chemistry:

$$C_6H_6 + O_2S(OH)Cl \rightarrow C_6H_5SO_3H + HCl$$

It forms no salts.

Fluorosulphuric Acid: This is made by the action of fuming sulphuric acid on KHF_2 or CaF_2 at ~ 250°C, or by the interaction of SO_3 and HF:

$$SO_3 + KHF_2 \rightarrow HSO_3F + KF; \; SO_3 + HF \rightarrow HSO_3F$$

It is also a colourless liquid (B.P. 169°C) and is only slowly hydrolysed by water. Its alkali metal salts are made by the action of SO_3 on metal fluorides at ~ 200°C. The acid is a very strong one.

Sulphuryl (Sulphonyl) Chloride: SO_2Cl_2 may be considered to have been derived from H_2SO_4 by the replacement of two OH^- groups by two chloro groups. Direct interaction of SO_2 and Cl_2 in the presence of camphor, charcoal or acetic anhydride as catalysts gives SO_2Cl_2. This is also obtained on refluxing chlorosulphonic acid with a little mercury sulphate or tin as a catalyst:

$$SO_2 + Cl_2 \rightarrow SO_2Cl_2; \; 2HSO_3Cl \rightarrow SO_2Cl_2 + H_2SO_4$$

It is a fuming liquid (B.P. 69°C) which is slowly hydrolysed by water:

$$SO_2Cl_2 + 2H_2O \rightarrow H_2SO_4 + 2HCl$$

It is used in the syntheses of acid chlorides of organic acids:

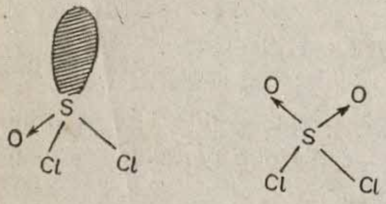
$$2CH_3COONa + SO_2Cl_2 \rightarrow 2CH_3COCl + Na_2SO_4$$

Thionyl Chloride (Sulphinyl Chloride): SO_2 and PCl_5 react to give a mixture of thionyl chloride, $SOCl_2$, (B.P. 78°C) and $POCl_3$(B.P. 107°C). $SOCl_2$ is recovered by fractional distillation: $SO_2 + PCl_5 \rightarrow SOCl_2 + POCl_3$.

Chlorine monoxide reacts with sulphur at −10°C to form $SOCl_2$. This is a colourless liquid which fumes in moist air and is hydrolysed by water:

$$SOCl_2 + 2H_2O \rightarrow SO_2 + H_2O + 2HCl$$

The structure of SO_2Cl_2 is roughly tetrahedral (sp^3 hybridisation of sulphur). Two sulphur lone pairs make the two coordinate links to the two oxygen. The other two are usual shared pair covalent bonds. In thionyl chloride, $SOCl_2$, the same roughly sp^3 hybridisation of sulphur is involved with one lone pair remaining intact on sulphur (19-XIV):



(19-XIV)

sp^3 hybridised sulphur	⇅	⇅	↑	↑
	3(sp^3)	3(sp^3)	3(sp^3)	3(sp^3)

The S−O bonds have double bond character due to overlap of filled oxygen $p-\pi$ orbitals with empty $d-\pi$ orbital of sulphur.

19.5.9. Amides of Sulphuric Acid: An acid amide is a compound derived from an acid by the replacement of an OH group by NH_2 group. Such replacement in H_2SO_4 results in sulphamic acid (NH_2-SO_2-OH) and sulphamide ($NH_2-SO_2-NH_2$).

Sulphamic Acid: It is prepared on a large scale by treating urea with fuming sulphuric acid:

$$CO(NH_2)_2 + SO_3 + H_2SO_4 \rightarrow 2NH_2SO_3H + CO_2$$

One of the older methods was to react hydroxylamine sulphate with SO_2 under pressure:

$$NH_2OH.H_2SO_4 + SO_2 \rightarrow NH_2.SO_3H + H_2SO_4$$

It is a crystalline non-hygroscopic solid. It is a strong acid and is used as a convenient primary standard in alkalimetry. It reacts quantitatively with HNO_2 giving nitrogen and sulphuric acid:

$$NH_2SO_3H + HNO_2 \rightarrow N_2 + H_2O + H_2SO_4$$

Determination of the sulphate so produced leads to estimation of nitrites. It has been used in agriculture as a selective weed keeler, and in dyestuff industry for destroying excess nitrite after diazotisation.

Sulphamide: It is obtained as colourless crystals by the action of ammonia gas on a solution of sulphuryl chloride:

$$SO_2Cl_2 + 4NH_3 \rightarrow SO_2(NH_2)_2 + 2NH_4Cl$$

It is purified by decomposing the silver salt $SO_2(NHAg)_2$ with HCl.

It functions as a biprotic bidentate NN donor ligand. This compound provided the first example of a purely inorganic optically active complex $Na[Rh(NH-SO_2-NH)_2(H_2O)_2]$ (page 223 ; Chapter 10; Part I).

19.6. SOME PROBLEMS CONCERNING SOLUBILITY PRODUCTS

In a saturated aqueous solution of a sparingly soluble ionic compound an equilibrium exists such that the product of the ion concentrations, each raised to a power equal to the coefficient of the ion in the solubility equation, is a constant. This constant is called the solubility product. This statement is valid only in very dilute solution. Thus the solubility of AgCl varies from 1.64×10^{-10} in aqueous solution to 2.40×10^{-10} in $0.04M$ KNO_3 solution. The failure of the concentration product to behave as a real constant is attributed to the inter-ionic attractions. The effect of these ions can be covered by writing the K_{SP} of AgCl in the following form:

$$\gamma_{Ag+} \times \gamma_{Cl-} \times [Ag^+] \times [Cl^-] = K'_{SP} = 1.64 \times 10^{-10}$$

γ_{Ag+} and γ_{Cl-} are the activity coefficients for the two ions. In very dilute solution the activity coefficients are close to unity because inter-ionic forces are extremely poor. In moderately concentrated solutions (eg : $0.04M$ KNO_3) the activity coefficients are significantly less than unity. Therefore in such solutions, concentrations of Ag^+ and Cl^- will increase so as to reach the K_{SP} of AgCl in aqueous solution. Thus while the solubility product may vary depending on the concentration of other non-common ions, the activity product (K'_{SP}) remains constant. In the presence of common ions the solubility of sparingly soluble ionic salts will change so as to maintain the K_{SP} constant.

Problem 1. Determine the solubility of AgCl in moles in three litres of 0.10*M* NaCl solution (K_{sp} of AgCl $= 1.6 \times 10^{-10}$).

The solubility of AgCl will be such as to maintain its K_{sp} constant.

$$\therefore \quad [\mathrm{Ag^+}] = \frac{1.6 \times 10^{-10}}{0.1} = 1.6 \times 10^{-9} \text{ moles/litre.}$$

$\therefore$ number of moles of AgCl in three litres of 0.10*M* NaCl $= 3 \times 1.6 \times 10^{-9} = 4.8 \times 10^{-9}$.

Problem 2. Barium (II) is being added to 0.1*M* fluoride solution. At what concentration of barium (II) will a precipitate of BaF_2 appear? ($K_{sp} = 2 \times 10^{-6}$)

A precipitate of BaF_2 will start to form when the product of Ba^{2+} and $[F^-]^2$ will exceed the K_{sp} of BaF_2.

$$BaF_2 \rightleftharpoons Ba^{2+} + 2F^-; \; K_{sp} = [Ba^{2+}] \times [F^-]^2 = 2 \times 10^{-6}$$

$$\therefore \quad [Ba^{2+}] = \frac{2 \times 10^{-6}}{0.1 \times 0.1} = 2 \times 10^{-4}M$$

Problem 3. What percentage of F^- (of Problem 2) will remain in solution when the concentration of Ba^{2+} ion is $1 \times 10^{-3}M$? (K_{sp} of $BaF_2 = 2 \times 10^{-6}$).

$$[F^-]^2 = \frac{K_{sp} \text{ of } BaF_2}{[Ba^{2+}]} = \frac{2 \times 10^{-6}}{1 \times 10^{-3}} = 2 \times 10^{-3}$$

$$\therefore \quad [F^-] = \sqrt{2 \times 10^{-3}} = 0.045M$$

$$\therefore \quad [F^-] \text{ in solution} = 0.1 - 0.045 = 0.055M$$

$$\therefore \quad \% [F^-] \text{ in solution} = \frac{0.055 \times 100}{0.1} = 55\%$$

Problem 4. Solubility of Ag_2CrO_4 is 6×10^{-5} moles/litre. What is its solubility product?

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$$

$$\therefore \quad K_{sp} = [Ag^+]^2 \times [CrO_4^{2-}] = (2 \times 6 \times 10^{-5})^2 \times (6 \times 10^{-5})$$
$$= 0.86 \times 10^{-12} \simeq 1 \times 10^{-12}$$

Problem 5. Solubility product of CaF_2 is 1.7×10^{-10}. Calculate its solubility in water.

$$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$$

$$\therefore \quad K_{sp} = [Ca^{2+}]\,[F^-]^2$$

Let *xM* per litre be the solubility.

$$\therefore \quad [Ca^{2+}] = x; \; [F^-] = 2x; \; Ksp = x \times (2x)^2$$

$$\therefore \quad 4x^3 = 1.7 \times 10^{-10} \quad \therefore \; x = 3.5 \times 10^{-4}M$$

Problem 6. The K_{sp} of ZnS is 4.5×10^{-24} while that of FeS is 1×10^{-19}. What would happen if H_2S is passed through a solution containing both Zn^{2+} and Fe^{2+} at $0.1M$?

If we wish to avoid precipitation of FeS the sulphide ion concentration must be less than:

$$[S^{2-}] = \frac{K_{sp}}{[Fe^{2+}]} = \frac{1 \times 10^{-19}}{0.1} = 10^{-18}M$$

A sulphide ion concentration of $\sim 10^{-19}M$ will ensure against any precipitation of FeS. For zinc (II) ion:

$$[Zn^{2+}] = \frac{K_{sp}}{[S^{2-}]} = \frac{4.5 \times 10^{-24}}{1 \times 10^{-19}} = 4.5 \times 10^{-5}M.$$

Thus we see that at 1×10^{-19} sulphide ion concentration only a small fraction of the original amount of zinc (II) remains in solution.

Problem 7. The solubility product of magnesium hydroxide, $Mg(OH)_2$, is 3.4×10^{-11}. What is the solubility of $Mg(OH)_2$ in pure water? What is the concentration of OH^- in the saturated solution? What is the pH of this solution?

$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$$

$K_{sp} = [Mg^{2+}]\ [OH^-]^2 = x \times (2x)^2 = 4x^3 = 3.4 \times 10^{-11}$ (x = solubility of $Mg(OH)_2$ in moles/litre)

$\therefore \quad x^3 = 0.8 \times 10^{-11} = 8.0 \times 10^{-12}\ ;\ x = 2 \times 10^{-4}M$

$\therefore \quad [OH^-] = 2x = 4 \times 10^{-4}M$

$\therefore \quad pOH = -\log [OH^-] = -\log 4 - (-4) \log 10 = 3.4$

$\therefore \quad pH = 14 - 3.4 = 10.6\ ;\ [pH + pOH = 14]$

Problem 8. K_{sp} of $PbSO_4$ is 1.8×10^{-8}. Calculate the solubility of $PbSO_4$ in (*a*) pure water; (*b*) $0.10M$ $Pb(NO_3)_2$ solution; (*c*) $1.0 \times 10^{-3}M$ Na_2SO_4 solution.

Ans: (*a*) $1.34 \times 10^{-4}M$; (*b*) $1.8 \times 10^{-7}M$; (*c*) $1.8 \times 10^{-5}M$.

Problem 9. A saturated solution of lanthanum iodate, $La(IO_3)_3$, in pure water has iodate concentration equal to 2.07×10^{-3} mole/litre at 25°C. What is the concentration of La^{3+}? What is the solubility product of $La(IO_3)_3$?

Ans: $0.69 \times 10^{-3}M$; $K_{sp} = 6.1 \times 10^{-12}$

K_{sp} values of a large number of sparingly soluble salts have been collected in Table 19.6. Solubilities of these salts in moles/litre as well as in gms./litre in their saturated aqueous solutions should be calculated as further exercises.

Table 19.6. Solubility Products of Some Sparingly Soluble Salts and Hydroxides

Anion	Salt	K_{sp}	Anion	Hydroxide/Salt	K_{sp}
Acetate	$AgCH_3COO$	2×10^{-3}	Hydroxide	$Al(OH)_3$	5×10^{-33}
Bromide	$AgBr$	1×10^{-13}		$Cr(OH)_3$	1×10^{-30}
	$PbBr_2$	5×10^{-6}		$Fe(OH)_3$	5×10^{-38}
	$TlBr$	3.6×10^{-6}		$Mg(OH)_2$	3.4×10^{-11}
	$CuBr$	5.9×10^{-9}		$Zn(OH)_2$	5×10^{-17}
Bromate	$AgBrO_3$	5.4×10^{-5}			
Carbonate	$BaCO_3$	1×10^{-9}	Iodide	AgI	1×10^{-16}
	$CaCO_3$	5×10^{-9}		TlI	8.9×10^{-8}
	$MgCO_3$	2×10^{-8}		CuI	1.1×10^{-12}
	$PbCO_3$	1×10^{-13}		PbI_2	1×10^{-8}
Chloride	$AgCl$	1.6×10^{-10}	Sulphate	$CaSO_4$	3×10^{-5}
	Hg_2Cl_2	1×10^{-18}		$SrSO_4$	7.6×10^{-7}
	$PbCl_2$	1.7×10^{-5}		$BaSO_4$	1.5×10^{-9}
	$TlCl$	1.9×10^{-4}		$RaSO_4$	4×10^{-11}
	$CuCl$	3.2×10^{-7}		$PbSO_4$	1.8×10^{-8}
Chromate	Ag_2CrO_4	1×10^{-12}	Sulphide	Ag_2S	1×10^{-49}
	$BaCrO_4$	2×10^{-10}		CdS	1×10^{-26}
	$PbCrO_4$	2×10^{-14}		CoS	1×10^{-21}
	$SrCrO_4$	3.6×10^{-5}		CuS	1×10^{-45}
				FeS	2×10^{-17}
Fluoride	BaF_2	2×10^{-6}		HgS	1×10^{-52}
	CaF_2	2×10^{-10}		MnS	1×10^{-13}
	PbF_2	4×10^{-8}		NiS	1×10^{-22}
				PbS	1×10^{-27}
				ZnS	1×10^{-23}

19.7. ISOLATION OF THE GROUP VIB ELEMENTS

19.7.1. Oxygen: It occurs in the free molecular form in air and in combined state in water and minerals. Different laboratory preparations involve the following reactions:

(1) MnO_2 catalysed thermal decomposition of $KClO_3$

$$2KClO_3 \xrightarrow[250^\circ C]{MnO_2} 2KCl + 3O_2$$

(2) reaction of Na_2O_2 with water gives NaOH, H_2O and O_2

(3) MnO_2 catalysed decomposition of H_2O_2

(4) thermal decomposition of oxides such as HgO, Ag_2O
(5) electrolysis of water.

On commercial scale oxygen is obtained from air. Air is liquefied under high pressure and at low temperature. Oxygen is then separated from nitrogen by fractional distillation. When liquid air is partially evaporated nitrogen (B.P. −196°C) escapes more rapidly than oxygen (B.P. −183°C). The oxygen rich fraction is evaporated, liquefied and again fractionally distilled giving satisfactory separation of the two major constituents of air. The gas is stored and shipped in strong steel cylinders under ~2000 lbs per square inch pressure.

19.7.2. Sulphur : It occurs in nature in the molecular form and also in combined state. There are huge deposits of native sulphur in Texas and Louisiana (USA) lying ~500 ft below the surface under layers of clay, limestone etc. It occurs as sulphide (*galena*, PbS; *iron pyrites*, FeS_2; *cinnabar*, HgS; *gypsum*, $CaSO_4 \cdot 2H_2O$ etc.) Native sulphur is extracted by digging holes from the surface down to the bed of sulphur, and then lowering three concentric pipes into the sulphur bed. Steam at a temperature of 160°C and under pressure is introduced through the outermost tube. Simultaneously a blast of hot air under high pressure is blown through the innermost pipe. The sulphur melts, and a frothy mixture of sulphur, air and water moves up the second annular space between the pipes. The mixture is collected and sulphur further purified by distillation. Sulphur is also economically extracted from the SO_2 liberated during roasting of metal sulphides. When SO_2 is passed over hot coke at ~1100°C it is reduced to sulphur.

19.7.3. Selenium : Most selenium is recovered from the SO_2 gas obtained during roasting metal sulphides. Small amounts of *metal selenides* accompany metal sulphides, and produce on roasting SeO_2. Selenium dioxide is deposited on cooling as colourless crystalline material. SeO_2 is then heated in a current of chlorine and the selenium chloride absorbed in water giving selenous acid. This solution is strongly acidified with HCl and reduced to elementary selenium by SO_2:

$$H_2SeO_3 + 2SO_2 + H_2O \rightarrow 2H_2SO_4 + Se$$

19.7.4. Tellurium : The chief source of tellurium is *bismuth telluride* Bi_2Te_3. The ore is fused with sodium carbonate when sodium telluride is formed:

$$Bi_2Te_3 + 3Na_2CO_3 \rightarrow 3Na_2Te + Bi_2O_3 + 3CO_2$$

The alkali telluride is extracted with water and oxidised by passing air, when tellurium precipitates:

$$2Na_2Te + 2H_2O + O_2 \rightarrow 4NaOH + 2Te$$

19.8. USES OF THE GROUP VIB ELEMENTS

Oxygen: Besides the vital role that oxygen plays in combustion, respiration and other biological processes it has several other interesting uses. It is used in oxy-acetylene welding torch and the oxy-hydrogen torch for cutting steel. It also serves to furnish a breathable atmosphere in high altitude flying and inside submarines. Liquid oxygen finds use in the laboratories for low temperature studies.

Sulphur: The major use of sulphur is in the manufacture of sulphuric acid. It is also used in the syntheses of other sulphur compounds such as CS_2, sulphur dyestuffs etc. It finds use in the manufacture of insecticides, gunpowder, fireworks etc.

Selenium: The variation in the electrical conductivity of elementary selenium with the intensity of light falling on it is utilised in the construction of selenium photocells. It is also used in the manufacture of ruby-red glass for signal lights.

Tellurium: Small amount of tellurium is sometimes added to lead pipes to increase resistance to corrosion.

19.9. ANALYTICAL REACTIONS OF THE GROUP VIB ELEMENTS

Oxygen can be absorbed in alkaline (KOH) pyrogallol. The gas may be burnt in hydrogen by passing over platinum sponge. The water formed can be absorbed in tubes containing concentrated H_2SO_4, anhydrous P_4O_{10} etc. Dissolved oxygen content of water may be determined by treating a solution of manganese (II) in water with alkali (in the absence of air) when MnO_2 is formed. The MnO_2 can then be determined iodometrically.

Sulphur compounds can be reduced to sodium sulphide by heating with sodium carbonate in a reducing flame. The sulphide can be recognised by its reaction towards silver (I) and lead (II) acetates giving black precipitates of sulphides. Sulphides may also be decomposed by acids to give H_2S. The H_2S may then be absorbed in alkali and the resulting alkali sulphide may be detected by reaction with sodium nitroprusside. A violet colour is produced:

$$Na_2[Fe(CN)_5NO] + Na_2S \rightarrow Na_4[Fe(CN)_5(NOS)]$$

Sulphur compounds can also be oxidised to sulphate by fusion with sodium peroxide. The sulphate can then be quantitatively estimated as $BaSO_4$.

Selenium compounds give a characteristic smell of raddish when heated on a charcoal block in a reducing flame. The volatile elementary selenium can be collected as a red deposit on a cold surface. Selenium compounds are usually reduced to the elementary state by a reducing agent such as SO_2 or N_2H_4 in concentrated HCl. The red precipitate is digested whereby it changes to an easily filterable gray form, and then weighed.

Tellurium compounds are also reduced to the element in $3M$ HCl by a *mixture* of SO_2 and N_2H_4, and can be weighed as Te.

STUDY QUESTIONS

1. Based on the electronic configuration present a concise account of the trends in the chemistries of the group VIB elements.

2. Oxygen and nitrogen are gases while sulphur and phosphorus are solids. How do you explain this?

3. The major differences between oxygen and sulphur are due to the differences in size, electronegativity and availability of 3*d*-orbital in sulphur. Comment.

4. The formulas of sulphuric and selenic acid are H_2SO_4 and H_2SeO_4 but telluric acid is H_6TeO_6. Comment.

5. Discuss the hybridised orbital models for the structures of SO_3 and SO_4^{2-} given the clues that SO_3 is triangular planar and SO_4^{2-} is tetrahedral and that both possess some double bond character in their S—O bonds.

6. Discuss the structure of thiosulphate ion.

7. What are peroxysalts? How do they differ from persalts?

8. Would you expect sulphur to form S^{6+} ion in its chemistry? What makes SF_6 so stable a compound?

9. Arrange the H_2X compounds of this group in order of increasing (*a*) acidity, (*b*) hydrogen bonding, (*c*) stability and (*d*) reducing power.

10. A solution of H_2S in water can act as (*a*) weak acid, (*b*) a dibasic acid, (*c*) a reducing agent and (*d*) a precipitating reagent. Write equations of each of these behaviours.

11. H_2S cannot precipitate NiS from a dilute acid solution of nickel sulphate but can precipitate CuS from an acidified cupric solution. Comment.

12. H_2S can act only as a reducing agent whereas SO_2 can act both as a reducing agent and an oxidising agent. H_2SO_4 can act only as an oxidising agent. Explain on the basis of electronic configuration and oxidation number.

13. Give an account of the syntheses and properties of H_2O_2. What is the common link in the structure of H_2O_2 and peroxysalts?

14. What is solubility product? Discuss its usefulness in analytical separation of different metal ions.

15. Calculate the solubility of CaF_2 in: (*a*) $0.1M$ $Ca(NO_3)_2$ and (*b*) $0.1M$ NaF ($K_{sp} = 2.0 \times 10^{-10}$).

Ans: (*a*) $\simeq 2 \times 10^{-5}M$, (*b*) $\simeq 2 \times 10^{-8}M$

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20

Group VIIB Fluorine, Chlorine, Bromine, Iodine and Astatine

The halogens occur in our nature only in combined state. The relative abundances are: F(0.08%); Cl(0.19%); Br(0.01%); I(10^{-4}%). Fluorine mostly occurs as *fluorspar* (CaF_2), *cryolite* (Na_3AlF_6) and *apatite* $Ca_5(PO_4)_3F$. Chlorine is present mostly in sea water as alkali and alkaline earth chlorides. It is also found in brine wells and as rock salt deposits. Bromine also occurs in sea water as bromide salts but to a much smaller extent. Iodine mostly occurs in sea weeds. Many marine plants adsorb iodide rather than bromide and chloride from sea water. Such sea weed is an important source of iodine. Bromine and iodine also accompany sodium chloride in brine wells to a small extent.

20.1. COMPARATIVE STUDY OF THE GROUP VIIB ELEMENTS

20.1.1. General Considerations : The group VIIB consists of fluorine, chlorine, bromine, iodine and astatine. Their chemistry follows from their electronic configurations, and hence from their position in the Periodic Table. All the elements have seven electrons in the ultimate quantum shell, the distribution being two electrons in the *s*-subshell and five in the *p*-subshell (Table 20.1). Some of the properties of the higher halogens can be explained only by considering participation of the *d*-orbitals in reactions and bonding.

The halogens are just one electron short of the next noble gas. The noble gas configuration can be achieved in two ways: (1) by gaining one electron from the reactive surrounding and thus forming uninegative halide ions, (2) by forming shared pair covalent bond. The tendency to accept one electron is so great that these elements possess the highest electron affinities in the Periodic Table (Table 20.1). Consequently one would expect that the elements would also register high ionisation potentials. Indeed the ionisation potentials are high, and expectedly decrease down the group. The fall in the ionisation potential induces some basic (cationic) properties in iodine and to some extent even in bromine. Compounds containing monopositive and tripositive iodine and monopositive bromine are known. Interestingly the first ionisation potential of iodine is about the same as that of mercury (Hg, 10.43 *ev*; I, 10.45 *ev*).

Table 20.1. Electronic Configurations and Some Properties of Group VIIB Elements

Element	Atomic Number	Electronic Configuration	Ionisation Potential (*ev*)	Electron Affinity	Electro-negativity
Fluorine	9	[He] $2s^2 2p^5$	17.42, 34.98 62.65, 87.14, 114.21	3.62	4.0
Chlorine	17	[Ne] $3s^2 3p^5$	13.01, 23.80, 39.90,53.50,67.80,	3.79	3.0
Bromine	35	[Ar] $3d^{10} 4s^2 4p^5$	11.84, 21.60, 35.90, 47.30, 59.70	3.56	2.8
Iodine	53	[Kr] $4d^{10} 5s^2 5p^5$	10.45, 19.09	3.28	2.5
Astatine	85	[Xe] $4f^{14} 5d^{10} 6s^2 6p^5$	......	....	2.2

The electron affinity of fluorine (3.62 *ev*) is less than that of chlorine (3.79 *ev*) although the reverse was to be expected. Note that the bond dissociation energy of F_2 (38 Kcal/mole) is less than that of Cl_2 (57 Kcal/mole). This indicates that F—F electron pair is less tightly held than Cl—Cl electron pair. In other words F atom will hold an extra electron giving F^- less strongly than a chlorine atom.

The electron affinity of chlorine being the highest in the series one would naturally predict that chlorine must also have the highest reduction potential ($M_2 + 2e \rightleftharpoons 2M^-$). However the picture is little more involved due to the following Born-Haber type cycles:

$$\begin{tikzcd}
\frac{1}{2}X_2(\text{solid}) \arrow[r, "\text{half heat}", "\text{of fusion}"'] & \frac{1}{2}X_2(\text{liquid}) \arrow[r, "\text{half heat}", "\text{of evaporation}"'] & \frac{1}{2}X_2(\text{gas}) \arrow[d, "\text{half heat of dissociation}"] \\
X^-(\text{hydrated}) & X^-(\text{gas}) \arrow[l, "\text{heat of}", "\text{hydration}"'] & X\,(\text{gas}) \arrow[l, "\text{electron}", "\text{affinity}"']
\end{tikzcd}$$

Since fluorine and chlorine are gases at room temperature the heats of fusion and evaporation can be ignored, so that the reduction potentials will depend on the sum of the heat of dissociation, electron affinity and heat of hydration. Note that the heats of fusion, evaporation and dissociation are positive (energy needs to be supplied) but the electron affinity and hydration energy are negative (energy released). The dissociation energy of the fluorine molecule (38 Kcals/mole) is much smaller than that of chlorine (57.1 Kcals/mole), and the heat of hydration of the fluoride ion (−121 Kcals/gm. ion) is more negative than that of the chloride ion (−87 Kcals/gm. ion). These two factors overweigh the slightly higher electron affinity of chlorine. *Therefore fluorine has the highest reduction potential and hence it is the most virulent oxidant known.*

The covalent radii and the ionic radii both increase (Table 20.2) down the group, although the increase is not very linear (as shown by a plot of the radii against period number of the halogens) along the series. This is understandable since, for example, between chlorine and fluorine the nuclear charge increases by 8 but between chlorine and bromine by as much as 18. This charge increase is coupled with the appearance of a *d*-block transition series in between chlorine and bromine. As a result the size of the bromide ion is smaller than might be expected. The radius of the astatide ion may also be explained on similar lines.

Table 20.2. Some More Properties of Group VIIB Elements

Element	Atomic Radius (A)	Ionic (X^-) Radius (A)	M.P. (°C)	B.P. (°C)	$E°$ volts ($X_2 + 2e \rightleftharpoons 2X^-$)
Fluorine	0.64	1.36	−233	−188	2.65
Chlorine	0.99	1.81	−102	−35	1.36
Bromine	1.14	1.95	−7	59	1.07
Iodine	1.33	2.16	113	183	0.54
Astatine	...	2.20			0.30

The size of the fluorine atom would indicate that the covalent bond making the F_2 molecule would be the shortest and hence the stablest. The bond dissociation energy should therefore be the highest. In reality bond dissociation energy falls regularly with increasing size from chlorine to iodine but fluorine has a much lower value than that of chlorine (Table 20.3). Two major lines of explanation have been advanced. Mulliken has suggested that alongwith an ordinary $p-p$ single bond between two chlorine atoms there is an overlap of a filled *p*-orbital of one chlorine with an empty *d*-orbital of the other chlorine. This kind of multiple bonding is not possible in fluorine since the latter is devoid of *d*-orbitals. Coulson argues that $p-p$ type σ-bond is enough to explain the anomaly provided we consider the relative magnitudes of the electron-electron repulsion and the electron-nucleus attractions. In Cl_2 bond length is larger than in F_2, and the interelectronic repulsions in the 2*p* orbitals of fluorine are considerably larger than the repulsions in the 3*p* orbitals of chlorine, and hence a smaller dissociation energy (Table 20.3) results for F_2.

Table 20.3. Bond Length and Energies of Halogen Molecules

Halogen Molecule	Bond Length (A)	Bond Dissociation Energy (K cals/mole)
F_2	1.42	38
Cl_2	1.99	57
Br_2	2.28	45.5
I_2	2.67	35.6

The colours of the halogen molecules show an interesting gradation from pale yellow (fluorine) through red (bromine) to violet (iodine). This is understandable from the molecular orbital picture (Fig. 5.8; Chapter 5). If we combine the outer shell atomic orbitals of two fluorine atoms, $2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$ then the electron distribution in the molecular orbitals of F_2 will be (taking x-axis as the bond axis):

$$\sigma_{2s}^2\ \sigma_{2s}^{*2}\ \sigma_{2px}^2 \pi_{2py}^2\ \pi_{2pz}^2\ \pi_{2py}^{*2}\ \pi_{2pz}^{*2}\ \sigma_{2px}^*$$

The σ_{2px}^* antibonding molecular orbital is lying vacant. The colours of the halogens arise from electronic transitions from an antibonding π^* orbital to the next σ_{2px}^* orbital. With increasing atomic number the gap between the π_{np}^* and the σ_{npx}^* orbitals narrows down so that the transition occurs at lower energy. Therefore in I_2 molecule the transition will require least energy and in F_2 the maximum energy. These energies are absorbed from the surrounding white light and we view substances in the transmitted light. Iodine absorbs yellow light (of lower energy) and transmits violet light (of higher energy) whereas fluorine absorbs violet light (of higher energy) and transmits yellow light (of lower energy) (compare Table 22.2. Chapter 22). Interesting in this context is the colour of iodine in various solvents. The colour is commonly violet (being that of the I_2 molecule) in CCl_4, CS_2 and aliphatic hydrocarbons but brown in oxygen—and nitrogen—carrying coordinating solvents like water, alcohol etc. Where the colour remains violet the electronic transition is the same as in I_2 itself. In the other coordinating type solvents charge transfer (donor-acceptor) type complexes between iodine and the solvents are formed and new absorption bands appear. Iodine also forms highly coloured complexes with polyhydric compounds such as starch. In this complex, of analytical importance, the iodine molecule appears to be seated in the interior of the starch helix.

20.1.7. Chemical Behaviour : *Hydrides:* All the halogens react with hydrogen to form volatile covalent hydrides. The reactivity towards hydrogen gradually falls from fluorine to iodine. HF and HCl are usually obtained by the action of H_2SO_4 on corresponding salts. But HBr and HI cannot be obtained this way since H_2SO_4 oxidises the acids to the halogens. The reducing strength of the hydrides increases from HF to HI. The usual method of obtaining these hydrides consists in treating a mixture of water and red phosphorus with bromine or iodine:

$$2P + 3Br_2 \rightarrow 2PBr_3\ ;\ PBr_3 + 3H_2O \rightarrow H_3PO_3 + 3HBr$$

Alternative methods are also available;

$$NaBr + H_3PO_4 \rightarrow NaH_2PO_4 + HBr;\ H_2 + Br_2 \rightarrow 2HBr$$

$$C_6H_6 + 2Br_2 \rightarrow C_6H_4Br_2 + 2HBr;\ H_2S + I_2 \rightarrow 2HI + S$$

The hydrides HCl, HBr and HI are gases at ordinary temperature with increasing boiling points but HF is a liquid (B.P. 19°C) because of association resulting from hydrogen bonding. All the hydrides ionise in aqueous solution due to solvation of the proton and the acidity increases from HF to HI. Electronegativity concept alone would predict the reverse order. The situation is complicated due to several factors. However the dominating factor is the decreasing dissociation energy from HF to HI, which again is due to increasing hydrogen-halogen separation (Chapter 8).

Halides: The variations in the character of binary halides along the Periodic Table have some superficial resemblance with the hydrides. Some alterations are noticed, however, due to greater size and polarisabilities of the halogens (particularly of iodine). Elements at the extreme left hand region of the Periodic Table form true saltlike (saline or ionic) halides. These halides are stabler than the corresponding hydrides. Ionic structures are most often forced by fluorine than by the other halogens. Other halides may show some deviation from idealised ionic structures. Like the hydrides again, elements belonging to the right hand area of the Periodic Table give rise to volatile covalent halides, the molecules being held by weak van der Waals' attraction. Dipolar effects leading to association are confined to HF, the effect being insignificant for the other halides. The halides formed by the central region elements of the Periodic Table (that is, the transition elements) do not have much parallellism with the hydrides of this region. Whereas the hydrides of the transition elements do not conform to definite stoichiometry. the halides do; e.g.: VCl_4, NbI_4, $[Mo_6Cl_8]^{4+}$, $ReCl_4$ etc. Since the hydrogen atom is much too small it can occupy interestices in metal structures. The halogens are much too large and much too electronegative to form interstitial type non-stoichiometric compounds.

Ionic halides have high melting points and boiling points because the forces holding together, for example, individual NaCl units in the crystal lattice are of the same order of magnitude as those holding Na^+ and Cl^- ions in NaCl (sublimation energy of NaCl solid to NaCl gas = 52 Kcals/mole; dissociation energy of NaCl into atoms = 98 Kcals/mole). With covalent halides these forces are much weaker (sublimation energy of CCl_4 solid to CCl_4 gas = 8 Kcals/mole; dissociation energy into C and Cl atoms = 311 Kcals/mole). Therefore covalent halides have low melting points and boiling points. The fluoride has generally the largest melting point and boiling point in a series of ionic halides of a given element. But for the covalent halides the iodide has the highest values because of larger molecular weight and consequently higher van der Waals' attraction (Chapter 5). In the halides of amphoteric elements such as Al (III), Sn(IV), Zn(II) the fluorides generally have the highest melting and boiling point with a sharp drop to the chloride (indicative of some change in bonding) and then a slow increase to the iodide via bromide (Fajans' rules, Chapter 5). CCl_4, CBr_4 and CI_4

have boiling points which are unexpectedly higher than the corresponding silicon halides. This anomaly has been explained in terms of partial multiple bonding of silicon and a consequent decrease in intermolecular forces. The *d*-orbital in silicon can participate in an overlap with a filled orbital of chlorine, bromine or iodine. But carbon cannot do this (Chapter 17). The heats of formation (energy released during formation of the compound from the elements) of halides tend to fall along a period of the Table in passing from metals to non-metals. Given the same metal the heat of formation again falls from fluoride to iodine.

Ionic halides conduct electricity in fused state but the covalent halides do not. Some non-metal halides such as BrF_3, ICl_3, $COCl_2$, NOCl, $POCl_3$ conduct electricity due to *autoionisation* processes of the type:

$$COCl_2 \rightleftharpoons COCl^+ + Cl^- \; ; \; 2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

Oxides and Oxyacids: The known oxides and oxyacids are given in Table 20.4. Notable in this list is the absence of any oxyacid of fluorine, presumably because fluorine is much too oxidising. Also note that there is no other oxide of fluorine beyond the oxidation number — 1. This negative oxidation number is only to be expected because fluorine is more electronegative (4.0) than oxygen (3.5) while the other halogens (Cl, 3.0 etc) are not. The other general points to be noted are: (1) with increase in oxidation number (that is, increase in electronegativity of a particular halogen the corresponding oxyacid becomes more acidic: (2) given the same oxidation number acidity of the oxyacid decreases with increasing atomic number, that is, with decreasing electronegativity (K_A: HClO, 3×10^{-8}; HBrO ~ 10^{-10}; HIO ~ 10^{-10}; $HClO_4$, very large); (3) with increasing oxidation number the halogen-oxygen links become more covalent and hence the oxidising power falls. For example, hypochlorites are stronger oxidants than perchlorates under usual laboratory conditions. Perchloric acid, however, becomes a violent oxidant under rather drastic reaction conditions. The extraordinarily stable chlorine-oxygen bonds are then destroyed. At elevated temperature perchloric acid behaves as a very strong oxidant towards organic matter.

Table 20.4. Oxides and Oxyacids of Halogens

Element	Oxidation Number						
	−1	+1		+3	+4	+5	+6	+7
Fluorine	OF_2 O_2F_2	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Chlorine	. . .	Cl_2O HClO	. . .	$HClO_2$	ClO_2	$HClO_3$	Cl_2O_6	Cl_2O_7 $HClO_4$
Bromine	. . .	Br_2O HBrO	. . .	. . .	BrO_2	$HBrO_3$	BrO_3	Br_2O_7 $HBrO_4$
Iodine	. . .	I_2O HIO	. . .	. . .	. . .	I_2O_5 HIO_3	. . .	HIO_4 H_5IO_6

acidity decreases

Role of the halides as ligands: Because of strong electronegative character and high electron affinity of the halogens much of the charge density of the metal-halide links in metal-halo complexes resides on the halide ions. As a result the splitting of the metal *d*-orbitals is poor and the halides occupy the weak field end of the spectrochemical series (Chapter 10). It may be recalled from SHAB concept (Chapter 8) that the halide ions can be arranged on the basis of polarisability etc. into ions of increasing and decreasing softness or hardness. On the Pearson rule that hard acids bind hard bases, and soft acids bind soft bases we have the following two series of stability sequences of metal-halide complexes:

(1) with hard acids (class 'a' acceptors): $I^- < Br^- < Cl^- < F^-$

(2) with soft acids (class 'b' acceptors): $I^- > Br^- > Cl^- > F^-$

Hydration of the halide ions: In accordance with Fajans' rules the smallest halide F^- must be the most heavily hydrated in solution and the largest iodide the least hydrated. So the hydration energy must fall down the group, and also for the same reason ionic conductance and ionic mobility must increase (Table 20.5). The reader should note that the halide ions in the hydration sphere are linked to water molecules through very weak electrostatic attraction between positive ends of dipolar H_2O and the negative halide ions.

Table 20.5. Hydration Energies. Ionic Mobilities and Ionic Conductances of Group VIIB Anions

Property	F^-	Cl^-	Br^-	I^-
Ionic Radius (A)	1.36	1.81	1.95	2.16
Hydration Energy (Kcals/gm. ion)	122	89	81	72
Ionic Conductance (ohms^{-1} cm^2)	46.6	65.3	67.3	66.3
Ionic mobility $\times 10^5$ (cm/sec./volt)	48.3	67.7	69.9	68.7

20.2. INTERHALOGEN COMPOUNDS

Halogens combine with each other to form interhalogen compounds. So far interhalogen compounds have been obtained between two different halogens. Taking A as the heavier halogen and B the lighter halogen, they are of the following types (Table 20.6).

Table 20.6. Types of Interhalogen Compounds

AB	AB_3	AB_5	AB_7
ClF	ClF_3	BrF_5	IF_7
BrF	BrF_3	IF_5	
IF	IF_3		
BrCl	ICl_3		
ICl			
IBr			

It may be noted that the number of B atoms is always odd, presumably to allow the interhalogen AB_n to attain a paired even electron system. The valence shell of A has even number of electrons.

The following points emerge from a scrutiny of the properties of the interhalogen compounds:

(1) The central atom has to expand its octet in order to accommodate more than one B group. In this game fluorine, being devoid of *d*-orbitals, cannot serve as the central atom.

(2) Although fluorine cannot serve as the central atom it helps the central atom to attain a high coordination number. This is due to its high electronegativity whereby excessive charge accumulation on the central atom is avoided.

(3) The highest interhalogen IF_7 is obtained in iodine—the largest halogen.

(4) The interhalogens lie almost on the linear plot of the boiling points of the halogens against the molecular weights of the halogens. This is a pointer that the interhalogens are covalently bonded.

(5) Since the interhalogens are made up of two halogens of differing electronegativity they often betray *autoionisation* in liquid state:

$$2\mathrm{ICl} \rightleftharpoons \mathrm{I}^+ + \mathrm{ICl_2}^- \ ; \ 2\mathrm{BrF_3} \rightleftharpoons \mathrm{BrF_2}^+ + \mathrm{BrF_4}^-$$

(6) The interhalogens are generally more reactive than the halogens because of the weakness of the covalent bond between two dissimilar electronegative elements. Their reactions, however, are like those of the halogens.

(7) Hydrolysis of an interhalogen produces a halide and an oxyhalide. The smaller and the more electronegative halogen forms the halide, and the larger and the less electronegative halogen forms the oxyhalide:

$$\mathrm{ICl} \xrightarrow{\mathrm{H_2O}} \mathrm{HOI} + \mathrm{HCl}$$

(8) The larger of the two halogens functions as the central atom.

The nature of the bonding in interhalogens can be understood on hybridisation model. In ClF_3 there are three covalent bonds which give chlorine a valence shell of ten electrons. Now invoking and sp^3d hybridisation

$$\begin{array}{lccccccccccc} & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow & & & \uparrow\downarrow & \uparrow\downarrow & \uparrow & \uparrow & \uparrow \\ \mathrm{Cl} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{hybridises to} & \text{———} & \text{———} & \text{———} & \text{———} & \text{———} \\ & 3s & 3p & 3p & 3p & 3d & & 3(sp^3d) & 3(sp^3d) & 3(sp^3d) & 3(sp^3d) & 3(sp^3d) \end{array}$$

chlorine can accommodate five electron pairs in its valence shell in a trigonal bipyramidal geometry. The three electrons in the three sp^3d hybrid orbitals overlap with the unpaired electrons of the three fluorine atoms. Two other points of the trigonal bipyramid are occupied by two chlorine lone pairs.

In IF_5 iodine has octahedral sp^3d^2 hybridisation, one hybrid orbital housing a lone pair and the other five orbitals (each with one electron) overlapping with fluorine unpaired electrons. The molecule assumes a square pyramidal shape (the sixth point of the octahedron being occupied by the lone pair). For IF_7 we have to involve a pentagonal bipyramid structure with sp^3d^3 hybridisation. Each iodine orbital with one electron then overlaps with unpaired electrons of the seven fluorine atoms.

The syntheses of the interhalogens, understandably, involve some direct interaction between the halogens, or between an interhalogen and the lighter halogen. Iodine monochloride (M.P. ~ 27°C) is obtained by the slow addition of the calculated amount of iodine in concentrated HCl or by the action of aqueous HCl on a mixture of potassium iodate and iodide:

$$KIO_3 + 2KI + 6KCl \rightarrow 3ICl + 3KCl + 3H_2O$$

Chlorine monofluoride is prepared by the reaction of moist chlorine with fluorine or by heating a mixture of chlorine and fluorine at ~250°C in a hollow copper block. The reaction mixture is cooled to −90°C to freeze out the unreacted chlorine and some ClF_3, and then ClF (M.P. −154°C; B.P. −101°C) is condensed in liquid air and purified by fractional distillation. Iodine trichloride is obtained as a solid from the reaction of ICl and Cl_2 at 100°C. Chlorine trifluoride is obtained by heating chlorine with excess of fluorine at ~280°C. Iodine pentafluoride (M.P. −8°C; B.P. 97°C) is formed on heating iodine and silver fluoride, or from the combination of iodine and fluorine gas. Iodine heptafluoride is made from the interaction of IF_5 and F_2 at ~250°C.

20.3. POLYHALIDES (INTERHALOGEN IONS)

Halogens or interhalogens combine with halide ions to form polyhalide ions (interhalogen ions). The polyhalides are known mostly as salts of strongly electropositive large cations, like the alkalies, heavy alkaline earths or large organic cations e.g. $[N(CH_3)_4]^+$. As yet no anhydrous acid of the polyhalide ions has been prepared. As in the interhalogens, here too the heavier halogen plays the role of the central atom. Some examples are included in Table 20.7. The AB_2^+ and AB_4^+ type polyhalogen cations arise out of the unusual dissociation of the interhalogens AB_3 and AB_5:

$$ICl_3 \rightleftharpoons ICl_2^+ + Cl^- \; ; \; 2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

$$2IF_5 \rightleftharpoons IF_4^+ + IF_6^-$$

In interhalogens we have all odd numbers of B atoms for a central A atom but in polyhalides for one A atom we have all even numbers of B atoms. The even number of the B atoms in AB_n^+ or AB_n^- allows the polyhalide ions to attain all paired spin system.

Table 20.7. Types of Polyhalide Anions and Polyhalogen Cations

AB_2^-	AB_4^-	AB_6^-	AB_8^-	AB_2^+	AB_4^+	ABC^-
I_3^-	ICl_4^-	IF_6^-	I_9^-	BrF_2^+	IF_4^+	$IBrCl^-$
ICl_2^-	I_5^-	I_7^-		ICl_2^+		
IBr_2^-	BrF_4^-					
$BrCl_2^-$						
Br_3^-						
I_2Cl^-						
I_2Br^-						
Br_2Cl^-						
Cl_3^-						

Ready formation of polyhalide is shown by the enhanced solubility of iodine in aqueous medium in the presence of iodide ions: $I_2 + I^- \rightleftharpoons I_3^-$. That the triodide ion is made up of one I^- and one I_2 is shown by its reaction with two moles of $Na_2S_2O_3$:$2Na_2S_2O_3 + KI_3 \rightarrow Na_2S_4O_6 + 2NaI + KI$. The pentaiodide, heptaiodide and the enneaiodide will react with 4, 6 and 8 moles of sodium thiosulphate respectively.

Polyhalides are formed by the action of a halogen on a halide, or by the action of an interhalogen such as ICl, ICl_3 or IBr on a halide. The salts are simply made by crystallising the halide salt in the presence of the appropriate halogen. $KI_3.H_2O$ forms black crystals.

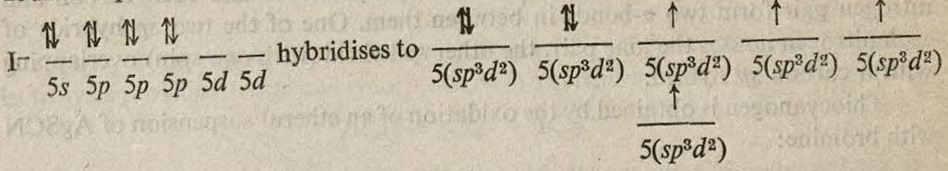
The stability against dissociation increases with the size of the central atom and the attached groups. The stability constants, *K*, of the following equilibrium:

$$AB + B^- \rightleftharpoons AB_2^-$$

have been determined for a number of polyhalides.

	Cl_3^-	Br_3^-	ICl_2^-	IBr_2^-	I_3^-
$K =$	0.01	17.8	167.0	370.0	725.0

The bonding in polyhalides follows the pattern of interhalogens. For example in ICl_4^- the central iodine has a total of $7 + 1 + 4 = 12$ electrons around itself. Iodine is sp^3d^2 hybridised:



The four hybrid orbitals with unpaired spins now overlap with chlorine orbitals (with one electron on each of the four chlorine atoms). The fifth and the sixth hybrid orbitals carry the lone pairs. The bond angles Cl—I—Cl are 90° so that ICl_4^- ion may be said to have a square planar arrangement of the four chlorine atoms around the iodine. The two lone pairs will point above and below the square plane.

20.4. THE PSEUDOHALOGENS

A few radicals are known which possess properties like the halogens. The important members of this group are —CN, —NCS, —N_3, —NCO, these being called pseudohalides. A pseudohalogen is a molecule, formed of electronegative heteroatoms, which resembles the halogens in its chemistry. Like the halides the pseudohalides give sparingly soluble precipitates with lead (II), silver (I) and mercury (I). Like the halogens the pseudohalogens can form ionic as well as covalent compounds. Like the halides the pseudohalides can also be oxidised to pseudohalogens:

$$4HSCN + MnO_2 \rightarrow Mn(SCN)_2 + (SCN)_2 + 2H_2O$$
$$4HCl + MnO_2 \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

The hydracids of the pseudohalogens are, however, weaker than the hydracids of the halogens. HCN is a very weak acid whereas HCl is a very strong acid in aqueous medium. This may be a reflection of the poor electronegativity of the pseudohalogens. The pseudohalides are stronger coordinating ligands than the halides. Cyanide is the strongest coordinating ligand known. This peculiarity in ligand properties must be ascribed to the ability of the electron deficient pseudohalides to form σ-bond (from the pseudohalide to the metal) as well as π-bond (from metal to the pseudohalide). The spectrochemical series including the halides and the pseudohalides run as under:

$$I^- < SCN \simeq < Br^- < Cl^- < F^- < NCO^- < NCSe^- < NCS^- < N_3^- \ll CN^-$$

Furthermore the pseudohalides, being made up of two hetero atom donors, can function as *ambidentate* ligands. For example class 'a' metals will form isothiocyanato complexes ($[Co(NCS)_4]^{2-}$) whereas class 'b' metals will form thiocyanato complexes ($[Pd(SCN)_4]^{2-}$) (Chapters 8 and 10).

Cyanogen can be obtained by a variety of methods: (*a*) by heating $Hg(CN)_2$ and $HgCl_2$: $Hg(CN)_2 + HgCl_2 \rightarrow Hg_2Cl_2 + (CN)_2$, (*b*) by the action of KCN on Cu^{2+}: $2Cu^{2+} + 4CN^- \rightarrow 2CuCN + (CN)_2$, (*c*) oxidation of HCN by air over a silver catalyst. Cyanogen is a very toxic and inflammable gas (B.P. −21°C). The structure is best described by a linear: $N \equiv C-C \equiv N$: with both the carbons being *sp* hybridised. The nitrogens are also *sp* hybridised and each carbon and nitrogen pair form two π-bonds in between them. One of the two *sp* hybrids of each nitrogen houses the lone pair, the other *sp* hybrid (with one spin) overlapping with a carbon *sp* hybrid.

Thiocyanogen is obtained by the oxidation of an etheral suspension of AgSCN with bromine:

$$2AgSCN + Br_2 \rightarrow 2AgBr + (SCN)_2$$

Solid $(SCN)_2$ is obtained by evaporating the ether solution and cooling to −70°C. It melts at −2°C to a yellow oil.

20.5. BASIC PROPERTIES OF THE HALOGENS

It is well established that in a group metallic character (cation formation) increases with increasing atomic number. It is gratifying to note that this generalisation holds even in this group of the most electronegative elements. Leaving aside astatine basic properties appear in iodine and to a limited extent even in bromine.

Note that the ionisation potential decreases down the group. Iodine has a potential value close to that of mercury (I, 10.45 *ev*; Hg, 10.43 *ev*). Although iodine on the whole is to be regarded as a non-metal the appearance of metallic character is indicated by its distinct conductivity compared to the other halogens:

Element	Chlorine	Bromine	Iodine
Specific conductivity of liquid halogen ($ohms^{-1}$, cm.)	$< 10^{-16}$	10^{-10}	5×10^{-5}

Cationic iodine is encountered in unipositive and in tripositive states.

20.5.1. Unipositive Iodine : This oxidation state is stabilised by complexation through pyridine. When silver nitrate and iodine are treated in chloroform in the presence of pyridine the following reaction occurs:

$$AgNO_3 + I_2 + 2py \rightarrow AgI + [I(py)_2]NO_3$$

After removal of the insoluble silver iodide the dipyridino iodine (I) nitrate is precipitated by the addition of ether. That the compound contains iodine (I) is proven by two experiments: (*a*) The compound reacts with iodide ion to liberate one iodine molecule: $I^- + I^+ \rightarrow I_2$ which can be quantitatively estimated with thiosulphate: $2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$. (*b*) Electrolysis of the compound in chloroform liberates iodine at the cathode: $2I^+ + 2e \rightarrow I_2$.

Powdered silver benzoate, $AgC_7H_5O_2$, reacts with quinoline and powdered iodine in chloroform medium to furnish pale yellow crystals of benzoato (quinoline) iodine (I):

$$AgC_7H_5O_2 + I_2 + C_9H_7N \rightarrow [I(C_9H_7N)(C_7H_5O_2)] + AgI$$

Iodine monochloride in fused state conducts electricity. On electrolysis iodine is liberated at the cathode, and both iodine and chlorine at the anode. These observations are accountable on the basis of the following ionisation:

$$2ICl \rightleftharpoons I^+ + ICl_2^-$$

20.5.2. Tripositive Iodine : The interhalogen ICl_3 conducts electricity and on electrolysis provides iodine and chlorine at both electrodes. Hence the ionisation is:

$$2ICl_3 \rightleftharpoons ICl_2^+ + ICl_4^-$$

Iodine can be oxidised by fuming nitric acid in the presence of acetic anhydride to give iodine triacetate. If this is electrolysed with silver electrodes one equivalent of AgI is formed at the cathode for every three Faradays of electricity:

$$I(CH_3COO)_3 \rightleftharpoons I^{3+} + 3CH_3COO^-$$
$$I^{3+} + 3e \rightleftharpoons \tfrac{1}{2}I_2$$

The compound liberates iodine from iodide ion according to the equation:

$$I^{3+} + 3I^- \rightarrow 2I_2$$

20.5.3. Unipositive Bromine : The unipositive bromine complexes $[Br(py)_2]NO_3$ and $[Br(py)_2]ClO_4$ have been synthesised using methods similar to those for unipositive iodine complexes. One molecule of the complex liberates one molecule of iodine:

$$Br^+ + 2I^- \rightarrow Br^- + I_2$$

Stabilisation of these positive oxidation states of the halogens cannot be undertaken in aqueous solution because of the reactions of the following type:

$$I^+ + OH^- \rightarrow HOI \; ; \; 2HOI + OI^- \rightarrow IO^-_3 + 2H^+ + 2I^-$$

20.6. PECULIARITIES OF FLUORINE

Fluorine differs markedly from the other halogens. Much of the peculiarities arise from its small size, extreme electronegativity and absence of low-lying *d*-orbitals. The major points of interest are:

1. It is the most electronegative element.

2. The electronegativity of fluorine introduces polarity in HF which in turn leads to association via hydrogen bonding.

3. Fluorine brings about the maximum coordination number of other elements. This is because of the small size of the atom and its extreme electronegativity. Both these factors permit a maximum number of small fluorine atoms around a central atom without accumulation of excessive negative charge on the central atom. Examples are SF_6, OsF_6, $[SiF_6]^{2-}$, IF_7 etc.

4. The solubilities of some of its salts are abnormal. Whereas silver chloride, bromide and iodide are insoluble in water, silver fluoride is highly soluble.

5. Among the halides of a given element the fluorides have the greatest tendency to ionise. AlF_3 and SnF_4, earlier thought to be ionic, are now considered to be polymeric (Part I, page 342).

6. Bond dissociation energy of the F_2 molecule is much lower than that of Cl_2 molecule.

7. Where chlorine and fluorine compounds of the same type occur, the fluorine compound is invariably the more stable one. Thus UF_6 is stabler than UCl_6, BF_4^- is stabler than BCl_4^-. NF_3 is non-explosive but NCl_3 is violently explosive.

20.7. COMPOUNDS OF THE GROUP VIIB ELEMENTS

20.7.1. Oxides of the Halogens : *Fluorine monoxide*, F_2O, is obtained as a gas (B.P. −145°C) by the interaction of fluorine on alkali solution:

$$2F_2 + 2NaOH \rightarrow 2NaF + H_2O + F_2O$$

Chlorine Monoxide, Cl_2O, (a yellowish-red gas) is made by passing chlorine over freshly precipitated mercuric oxide:

$$2Cl_2 + 2HgO \rightarrow HgO.HgCl_2 + Cl_2O$$

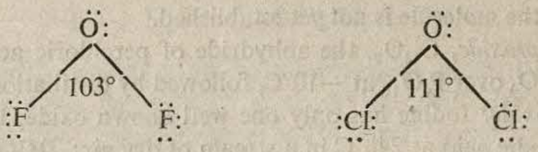
It is the anhydride of hypochlorous acid since it reacts with water to give HOCl:

$$Cl_2O + H_2O \rightarrow 2HOCl$$

It tends to explode under various conditions to give Cl_2 and O_2.

Bromine Monoxide, Br_2O, is the anhydride of hypobromous acid, and is obtained by the action of bromine on freshly prepared mercuric oxide.

All three monoxides are covalent with sp^3 hybridisation of the oxygen. Two of these hybrid orbitals accommodate two lone pairs and the other two (with one electron on each) overlap with *p*-orbitals of the halogens (also with one electron). The halogen-oxygen-halogen bond angle should be ideally 109° but in reality varies due to the repulsions of the bonding pairs. Since fluorine is more electronegative than chlorine the bond pairs of F_2O have less electron density in the vicinity of oxygen than the bond pairs of Cl_2O and hence the F—O—F angle is less than Cl—O—Cl angle (20-I). The bond-pair repulsion in Cl_2O is more than that in F_2O.



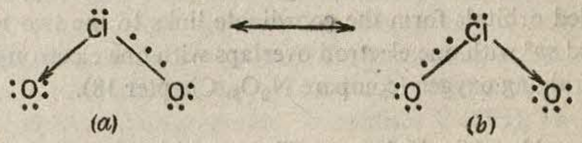
(20-I)

Chlorine dioxide, ClO_2, is prepared by treating silver chloride at 90° with dry chlorine and by cooling the evolved ClO_2 (B.P. 11°C): $2AgClO_3 + Cl_2 \rightarrow 2AgCl + 2ClO_2 + O_2$. Another useful method is the reaction of potassium chlorate and oxalic acid: $2KClO_3 + 2H_2C_2O_4 \rightarrow K_2C_2O_4 + 2H_2O + 2ClO_2 + CO_2$. This is a yellowish gas, is an odd electron molecule but does not dimerise. Its aqueous solution gives both chlorite and chlorate ions:

$$2ClO_2 + H_2O \rightarrow HClO_2 + HClO_3$$

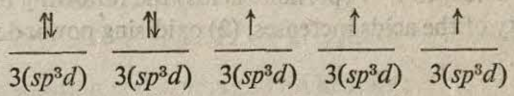
alkaline medium

The molecule has a O—Cl—O angle ~ 117° and O—Cl bond distance 1.49A (single bond covalent radius gives $0.66 + 0.99 = 1.65$A). Pauling represents the molecule as a resonance hybrid of three-electron structures (20-II; a and b):



(20-II)

These resonating forms are compatible with sp^3d hybridisation of the chlorine atom:



One orbital has the lone pair and another makes the coordinate link to one oxygen. The third and the fourth sp^3d orbitals make a sigma and also a π-bond with the other oxygen. The odd electron remains located on the fifth sp^3d orbital. Chlorine thus has a valence shell of $7 + 1 + 1 = 9$ electrons. The two structures become equivalent by resonance. An alternative scheme of the three-electron structures with the odd electron residing on an oxygen orbital may also be worked out.

Bromine dioxide, BrO_2, is obtained by passing electric discharge through a mixture of bromine and oxygen. Hydrolysis gives bromide and bromate:

$$6BrO_2 + 3H_2O \rightarrow HBr + 5HBrO_3$$

Dichlorine Hexoxide, Cl_2O_6, is obtained as a result of mixing ClO_2 and ozone at 0°C. It is also obtained by the ultraviolet irradiation of ClO_2. Molecular weight determination in CCl_4 points to the dimeric formula. It is a red liquid that reacts with alkalies to give chlorates and perchlorates:

$$Cl_2O_6 + 2NaOH \rightarrow NaClO_3 + NaClO_4 + H_2O$$

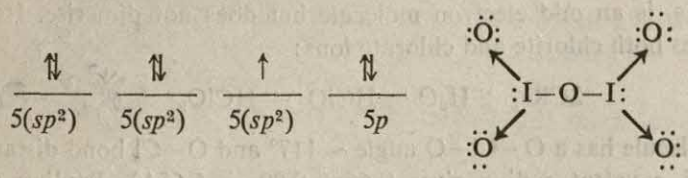
The structure of the molecule is not yet established.

Chlorine Heptoxide, Cl_2O_7, the anhydride of perchloric acid is obtained by dehydrating $HClO_4$ over P_4O_{10} at −10°C, followed by distillation at 85°C.

Iodine Pentoxide: Iodine has only one well known oxide, I_2O_5, made by the dehydration of iodic acid at 240°C in a stream of dry air: $2HIO_3 \rightarrow I_2O_5 + H_2O$. The reaction shows that it is the anhydride of iodic acid. It is an oxidising agent, oxidising H_2S, HCl and CO, itself being reduced to iodine:

$$5CO + I_2O_5 \rightarrow I_2 + 5CO_2$$

The molecule has the following planar structure (20-III): Each iodine is sp^2 hybridised with the seven electrons poised as:



(20-III)

The two sp^2 filled orbitals form the coordinate links to the two terminal oxygen atoms. The third sp^2 with one electron overlaps with one electron in *sp* hybridised orbital of the bridging oxygen (compare N_2O_5, Chapter 18).

20.7.2. Oxyacids of the Halogens : The oxyacids of the halogens can be subdivided under hypohalous acids, halous acids, halic acids and perhalic acids (Table 20.8). With increase in the oxidation number of the central halogen atom from + 1 (halous acids) to + 7 (perhalic acids) the following effects are observed: (1) thermal stability of the acids increases, (2) oxidising power decreases and (3) acid strength increases.

Table 20.8. Oxyacids of the Halogens

Chlorine	Bromine	Iodine
$HClO$	$HBrO$	HIO
$HClO_2$	. . .	. . .
$HClO_3$	$HBrO_3$	HIO_3
$HClO_4$	$HBrO_4$	HIO_4, H_5IO_6

Hypohalous Acids: These are formed in aqueous solution on reacting the halogens with water:

$$Cl_2 + H_2O \rightarrow HOCl + HCl$$

The reaction is facilitated by alkali when hypohalites are formed. Aqueous solution of the acids can also be obtained by shaking freshly precipitated HgO with the halogens in aqueous suspension:

$$2Cl_2 + 2HgO + H_2O \rightarrow HgO.HgCl_2 + 2HOCl$$

Sodium hypochlorite, an important cotton-bleaching agent, is obtained on a large scale by electrolytic oxidation of brine. As the electrolysis continues the catholyte becomes alkaline due to removal of H^+ ions from water:

$$H_2O \rightarrow H^+ + OH^-;\ 2H^+ + 2e \rightarrow H_2$$

At the anode chloride ions are oxidised to chlorine:

$$NaCl \rightarrow Na^+ + Cl^-\ ;\ 2Cl^- \rightarrow Cl_2 + 2e$$

On agitating the electrolyte chlorine and alkali mix and sodium hypochlorite is formed:

$$2NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O$$

The overall result is the release of hydrogen at the cathode and production of NaOCl in solution. Earthen-ware trough usually serves as the container of the brine. Into this trough are fitted a series of graphite plates which divide the cell into many narrow compartments. The terminal graphite plates are connected to a D. C. source. The graphite plates act as cathode on one side and as anode on the other side. Hydrogen and NaOH are formed at one face of each graphite plate while Cl_2 is released on the opposite face. These react to form NaOCl. The temperature of the bath is kept around 25°C. On cooling sodium chloride crystallises first. On further cooling to −10°C sodium hypochlorite crystallises. Sodium hypochlorite is a strong oxidant. It oxidises $Fe(OH)_3$ to FeO_4^{2-}, Ag_2O to AgO and $Cr(OH)_3$ to CrO_4^{2-} ;

$$2Fe(OH)_3 + 3NaOCl + 4NaOH \rightarrow 2Na_2FeO_4 + 3NaCl + 5H_2O$$

$$Ag_2O + NaOCl \rightarrow 2AgO + NaCl$$

$$2Cr(OH)_3 + 3NaOCl + 4NaOH \rightarrow 2Na_2CrO_4 + 3NaCl + 5H_2O$$

Sodium hypochlorite solution is decomposed on heating:

$$3NaOCl \rightarrow NaClO_3 + 2NaCl$$

With HCl chlorine is evolved;

$$NaOCl + 2HCl \rightarrow NaCl + H_2O + Cl_2;\ OCl^- + 2H^+ + 2e \rightarrow H_2O + Cl^-$$

Hypochlorite is a good bleaching agent for cotton but is entirely unsuitable for silk and wool.

Bleaching Powder: This is produced when chlorine gas is passed over dry slaked lime. Its composition varies and is usually a mixture of calcium hypochlorite, calcium chloride and unreacted calcium hydroxide. The reaction is commonly depicted as:

$$Ca(OH)_2 + Cl_2 \rightarrow H_2O + CaCl(OCl)$$

On acidification bleaching powder gives HOCl which then reacts with HCl to produce chlorine. Bleaching powder is hydrolysed by water and loses chlorine and therefore it should be protected from moisture until it is put to use. The quantity of bleaching powder is determined on the basis of *available chlorine* liberated on reacting with an acid (HCl):

$$OCl^- + Cl^- + 2H^+ \rightarrow Cl_2 + H_2O$$

The available chlorine is usually determined by treating a suspension of the bleaching powder with an excess of KI and strongly acidifying with acetic acid:

$$OCl^- + 2I^- + 2H^+ \rightarrow Cl^- + I_2 + H_2O$$

The liberated iodine is then titrated with a standard thiosulphate solution:

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

On boiling an aqueous suspension of bleaching powder calcium chlorate and chloride are formed:

$$6Ca(OCl)Cl \rightarrow Ca(ClO_3)_2 + 5CaCl_2$$

Halous Acid: Only chlorous acid $HClO_2$ is known in solution. Sodium chlorite is best made by the action of Na_2O_2 on chlorine dioxide.

$$\begin{array}{c} Na_2O_2 + 2ClO_2 \rightarrow 2NaClO_2 + O_2 \\ \downarrow \text{heat} \\ NaClO_3 + NaCl \end{array}$$

In keeping with the increasing electronegativity of chlorine, chlorous acid ($K_A \sim 10^{-2}$) is stronger than hypochlorous acid ($K_A \sim 10^{-8}$). Chlorites are used as bleaching agents.

Halic Acids: Alkali metal chlorates are made by the electrolysis of hot alkali chloride solutions. Aqueous KCl (25%) is generally electrolysed at 25°C between a series of platinum foil electrodes which are close enough to allow the products of electrolysis to react. On cooling $KClO_3$ crystallises. The reaction may be viewed as production of KOCl as a first step followed by conversion to the chlorate at higher temperature:

$$3KOCl \rightarrow KClO_3 + 2KCl$$

When chlorine is passed into alkali hydroxide solution, hypochlorite and chloride are formed so long as alkali is present. On saturating the solution with chlorine the hypochlorite is rapidly converted into chlorate:

$$2NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O$$

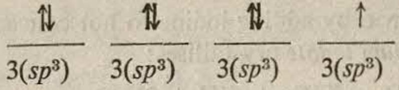
$$3NaOCl \rightarrow NaClO_3 + 2NaCl$$

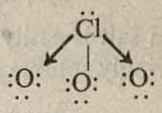
On heating a chlorate first melts and then decomposes to give a perchlorate and a chloride. The perchlorate, having a higher melting point solidifies but decomposes on further heating to give chloride and oxygen:

$$4KClO_3 \rightarrow 3KClO_4 + KCl; \; KClO_4 \rightarrow KCl + 2O_2$$

In the presence of MnO_2 decomposition of $KClO_3$ takes place at a lower temperature (~ 200°C) and quite smoothly. Chloric acid exists only in aqueous solution and is best made by treating barium chlorate with sulphuric acid and filtering off the barium sulphate.

The chlorate ion has a tetrahedral (sp^3) chlorine (20-IV):





(20-IV)

One sp^3 hybrid makes the lone pair and two others, with electron pairs, form the two coordinate links to two oxygen atoms. The third sp^3 hybrid with one electron overlaps with a p orbital of O^-. Since chlorine has d-orbitals there remains a scope for double bonding by the overlap of a filled oxygen p-orbital with an empty d-orbital of chlorine. The three oxygen will be equivalent through resonance. Because of one lone pair and three bond pairs the chlorate ion will have a pyramidal shape (cf: NH_3). One may take an alternative view of having the extra electron of the negative chlorate ion in sp^3 orbital so that all the four sp^3 orbitals have paired spins. In such a case chlorine will be linked to the three oxygens via coordinate bonds (see chapter 6; page 131).

When bromine is dissolved in excess in *hot* KOH solution a bromate and a bromide result. *Potassium bromate* being much less soluble than bromide crystallises on cooling. Bromic acid like chloric acid exists only in aqueous solution and is obtained in solution by treating the barium salt with sulphuric acid. Bromates are stronger oxidants than chlorates and are used in analysis for different oxidimetric titrations:

$$BrO_3^- + 6H^+ + 6e \rightleftharpoons Br^- + 3H_2O$$

$$BrO_3^- + 3H_3AsO_3 \xrightarrow{HCl} Br^- + 3H_3AsO_4$$

$$2BrO_3^- + 3N_2H_4 \xrightarrow{HCl} 2Br^- + 3N_2 + 6H_2O$$

$$BrO_3^- + 6[Fe(CN)_6]^{4-} + 6H^+ \rightarrow Br^- + 6[Fe(CN)_6]^{3-} + 3H_2O$$

After the quantitative oxidation of the above reducing agents (H_3AsO_3, N_2H_4 etc.), next additional drop of the bromate solution results in the oxidation of the bromide ion to bromine. The endpoint of the titration can be detected by the appearance of the yellow colour of bromine

$$BrO_3^- + 5Br^- + 6H^+ \rightleftharpoons 3Br_2 + 3H_2O$$

or better by the discharge of the colour of some organic indicator such as methyl orange or methyl red. (Also see sections 15.9 and 16.7).

Iodic acid is an important oxyacid of iodine. It is best prepared by boiling iodine with ten times its weight of fuming nitric acid. The nitric acid is finally removed at 200°C, the residue is dissolved in warm water when the free acid separates on cooling as colourless crystals:

$$3I_2 + 10HNO_3 \rightarrow 6HIO_3 + 10NO + H_2O$$

Iodic acid is also formed by passing chlorine into a suspension of iodine in water:

$$I_2 + 5Cl_2 + 6H_2O \rightarrow 2HIO_3 + 10HCl$$

The potassium salt is easily obtained by adding iodine to hot concentrated alkali when the sparingly soluble *potassium iodate* crystallises:

$$3I_2 + 6KOH \rightarrow KIO_3 + 5KI + 3H_2O$$

This is also formed by heating iodine with a concentrated solution of $KClO_3$ in presence of little HNO_3:$2KClO_3 + I_2 \rightarrow 2KIO_3 + Cl_2$. Addition of barium nitrate to a solution of KIO_3 precipitates barium iodate, $Ba(IO_3)_2$. Potassium iodate is also a good oxidant and is used in many oxidimetric titrations. However its redox behaviour is different from that of potassium bromate. In presence of 0.1–2*M* HCl iodate is reduced to iodine:

$$2IO_3^- + 5H_3AsO_3 + 2H^+ \rightarrow I_2 + 5H_3AsO_4 + H_2O$$

$$HIO_3 + 5HI \rightarrow 3I_2 + 3H_2O\ ;\ 2HIO_3 + 5H_2S \rightarrow I_2 + 6H_2O + 5S$$

In presence of 3–9*M* HCl reduction proceeds to the stage of ICl:

$$IO_3^- + 6H^+ + Cl^- + 4e \rightleftharpoons ICl + 3H_2O$$

Potassium biiodate, $KH(IO_3)_2$ (also written as KHI_2O_6 or $KIO_3.HIO_3$), an important acidimetric standard, is obtained by mixing hot concentrated solutions of KIO_3 and HIO_3 in the presence of a few drops of HCl. On cooling potassium biiodate crystallises. It is also obtained by decomposing barium iodate $Ba(IO_3)_2$ with potassium bisulphate. The precipitated barium sulphate is removed and the filtrate on concentration gives crystals of the biiodate. It behaves as a strong acid and is used as a primary standard for standardisation of bases. Potassium biiodate KHI_2O_6 exists in the solid state due to favourable lattice energy and low solubility in aqueous medium. Outside this there is no ground to believe that iodic acid is dimerised. In solution KHI_2O_6 is wholly dissociated into K^+, H^+ and IO_3^- ions.

Perhalic Acids: Potassium perchlorate is prepared by heating potassium chlorate around 500°C in a silica vessel for several hours: $4KClO_3 \rightarrow 3KClO_4 + KCl$. Treatment with cold water dissolves the chloride leaving behind the sparingly soluble potassium perchlorate. This is also obtained by electrolytic oxidation of aqueous $NaClO_3$ to $NaClO_4$ being followed by the addition of KCl when sparingly soluble $KClO_4$ precipitates.

$$NaClO_3 \longrightarrow \underset{\text{(cathode)}}{Na^+} + \underset{\text{(anode)}}{ClO_3^-}\ ;\quad H_2O \rightarrow \underset{\text{(cathode)}}{H_2} + \underset{\text{(anode)}}{\tfrac{1}{2}O_2}$$

$$ClO_3^- + \tfrac{1}{2}O_2 \rightarrow ClO_4^-\ \text{(anode)}$$

It is desirable that the oxygen discharged on the anode be available for reaction with chlorate ion. It is therefore essential to employ bright platinum anode (which has a high oxygen overvoltage). Platinised platinum allows ready evolution of oxygen gas and thus the yield falls. In practice sodium chlorate is electrolysed at 30-60°C in an open cell between bright platinum anode and iron cathode. The free acid is obtained by distilling potassium perchlorate with concentrated sulphuric acid:

$$KClO_4 + H_2SO_4 \rightarrow KHSO_4 + HClO_4$$

The acid forms several hydrates, the monohydrate having a melting point 50°C (Chapter 8). The monohydrate is best represented as $[H_3O]$ $[ClO_4]$. It is a very strong acid in aqueous solution.

The perchlorate ion is tetrahedral with sp^3 hybridised chlorine having a valence shell of $7 + 1 = 8$ electrons. These 8 electrons in four pairs are located in the four hybrid orbitals, these making coordinate links to the four oxygen atoms. The chlorine-oxygen bonds have considerable double bond character due to overlap of filled oxygen orbitals with empty *d*-orbitals of chlorine. The perchlorate ion is isomorphous with permanganate, perrhenate and fluoroborate ions. The strong chlorine-oxygen bonds must be the reason for its weak oxidising ability under ordinary conditions. However it becomes a violent oxidant only in contact with organic substances at elevated temperatures.

Perbromate has recently been obtained by fluorine oxidation of bromate in alkaline medium:

$$KBrO_3 + 2KOH + F_2 \rightarrow KBrO_4 + 2KF + H_2O$$

On heating above 275°C $KBrO_4$ decomposes to $KBrO_3$ and oxygen.

Periodic acid occurs in several compositions but with the same oxidation number + 7. A white precipitate of *disodium paraperiodic* acid is obtained when chlorine is passed through a boiling solution of iodine in excess alkali:

$$18NaOH + I_2 + 7Cl_2 \rightarrow 2Na_2H_3IO_6 + 14NaCl + 6H_2O$$

Silver paraperiodate is obtained when a suspension of the above sodium salt is treated with $AgNO_3$:

$$Na_2H_3IO_6 + 5AgNO_3 \rightarrow Ag_5IO_6 + 2NaNO_3 + 3HNO_3$$

The Ag_5IO_6 is decomposed with an aqueous solution of chlorine when silver chloride precipitates and the free periodic acid H_5IO_6 remains in solution:

$$Ag_5IO_6 + 10Cl_2 + 10H_2O \rightarrow 4H_5IO_6 + 20AgCl + 5O_2$$

On heating to 100°C in vacuo H_5IO_6 changes to HIO_4, the *metaperiodic acid.*

Perchlorate and paraperiodate (the dominating forms of the periodic acid) are different in their compositions. Higher member of a particular group of the Periodic Table generally can accommodate more oxo ions around itself because of its larger size. The periodates are strong oxidants, oxidising manganese (II) to permanganate and liberating iodine from iodide.

$$2MnSO_4 + 5H_5IO_6 \rightarrow 2HMnO_4 + 5HIO_3 + 2H_2SO_4 + 7H_2O$$

$$KIO_4 + 7KI + 8HCl \rightarrow 8KCl + 4I_2 + 4H_2O$$

Also recall that periodates and tellurates, being negative groups with the central atom in the highest oxidation state, are excellent vehicles for stabilising high oxidation states of silver (III) etc (Chapter 10).

The structure of IO_6^{5-} is octahedral, the central atom using sp^3d^2 hybridisation.

⇅	↑	↑	↑	↑	↑
$5(sp^3d^2)$	$5(sp^3d^2)$	$5(sp^3d^2)$	$5(sp^3d^2)$	$5(sp^3d^2)$	$5(sp^3d^2)$

It may then be assumed that one of the oxygen atoms is held by a coordinate link and the other five O^- ions by shared pair covalent bonds. Alternatively one may assume a valence shell of $7 + 5 = 12$ electrons around iodine. Eeach sp^3d^2 hybrid then carries one pair which makes co-ordinate bonds to the six oxygen atoms.

20.8. ASTATINE

Astatine-211 was prepared by bombarding bismuth-209 with alpha particles:

$${}^{209}_{83}\mathrm{Bi} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{211}_{85}\mathrm{At} + 2\,{}^{1}_{0}n$$

The method of its synthesis coupled with the distinctive chemical properties, which in many cases are similar to those of iodine, established its identity as element-85 belonging to group VIIB. Astatine-211 undergoes branched decay: (*a*) 60% by orbital electron capture to polonium-211 which immediately decays to stable lead-207 and (*b*) 40% by alpha emission to bismuth-207:

$${}^{307}_{83}\mathrm{Bi} \xleftarrow{\alpha} {}^{211}_{85}\mathrm{At} \xrightarrow[\text{orbital electron capture}]{\text{7.5 hr. half life}} {}^{211}_{84}\mathrm{PO} \xrightarrow{\alpha} {}^{207}_{82}\mathrm{Pb}$$

Astatine-218 has been identified in a natural source. Polonium-218 undergoes (in addition to alpha decay) beta branching to the extent of $5 \times 10^{-2}\%$ to produce astatine-218 (half life 2 seconds), which is an alpha emitter.

The properties of this short lived element have been studied by tracer technique with the aid of carriers. There are several oxidation states of astatine. Strong reducing agents such as SO_2 or Zn in acid medium produces a negative state believed to be the astatide At^- ion because it coprecipitates with insoluble iodides such as of silver (I), thallium (I) etc. The potential $At + e \rightleftharpoons At^-$ is 0.3 volts. The zero oxidation state, that is astatine itself, is characterised by high volatility. It resembles iodine in its high extractibility into organic solvents of which two groups can be distinguished. CCl_4, C_6H_6 and hydrocharbons forming one group and the other group including ethers, tributylphosphate and other oxygenated solvents. Like the polyhalides, astatine also forms $AtCl_2^-$, $AtCl_4^-$ etc. Strong oxidants such as $K_2S_2O_8$, HOCl, Ce^{4+}, $NaBiO_3$ convert astatine to a form which can be precipitated with silver (I), lead (II) as astatate, AtO_3^-, and can be carried down with silver iodate.

20.9. ISOLATION OF THE ELEMENTS

Fluorine occurs in nature as fluorides of the strongly basic elements: *fluorspar* (CaF_2), *cryolite* (Na_3AlF_6) etc. Chlorine and bromine mostly occur as alkali and alkaline earth halides in sea water and inland lakes and brine wells. Iodine is mostly found in sea weeds which absorb minute quantities of sodium and potassium iodide.

In all their sources the halogens are present as anions. Consequently all methods of preparations of the free halogens involve oxidation of the halide ions. This oxidation can be effected for all the halogens by electrolytic methods, and for chlorine, bromine and iodine by the use of strong oxidising agents as well.

20.9.1. Fluorine: Fluorine can be obtained by the anodic oxidation of fluoride ion. Fused KHF_2 is electrolysed at 250°C (M.P. KHF_2, 239°C) in an electrically heated copper vessel with graphite electrodes. Instead of fused KHF_2, a mixture of anhydrous HF and KHF_2 may also be employed. The following reactions occur:

$$KHF_2 \xrightarrow{\text{(fused)}} K^+ + H^+ + 2F^- \xrightarrow{\text{(electrolysis)}} \left[\begin{array}{l} \xrightarrow{\text{cathode}} 2H^+ + 2e \rightarrow H_2 \\ \xrightarrow[\text{anode}]{} 2F^- \rightarrow F_2 + 2e \end{array}\right.$$

At the cathode H^+ is more easily discharged than K. All traces of moisture must be removed since fluorine reacts with water with gusto:,

$$2H_2O + 2F_2 \rightarrow 4HF + O_2$$
$$3H_2O + 3F_2 \rightarrow 6HF + O_3$$

Fluorine is generally handled in copper or steel vessels but it can be studied in glass equipments provided the gas is scrupulously freed from HF which is the reagent that etches glass. This can be achieved by absorbing the HF in fused NaF or KF.

The following E° values convince us that it is easier to oxidise H_2O to oxygen than it is to oxidise F^- to F_2 and also that it is easier to reduce H^+ than it is to reduce Na^+ or K^+ ions:

$$\begin{array}{rl} F_2 + 2e \rightleftharpoons 2F^- \;; & E^\circ = +\ 2.65 \text{ volts} \\ O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O; & E^\circ = +\ 1.23 \text{ volts} \\ 2H^+(10^{+7}M) + 2e \rightleftharpoons H_2 \;; & E^\circ = -\ 0.41 \text{ volts} \\ Na^+ + e \rightleftharpoons Na \;; & E^\circ = -\ 2.71 \text{ volts} \\ K^+ + e \rightleftharpoons K \;; & E^\circ = -\ 2.92 \text{ volts} \\ Cl_2 + 2e \rightleftharpoons 2Cl^- \;; & E^\circ = +\ 1.36 \text{ volts} \end{array}$$

Early failures to obtain fluorine by the electrolysis of an aqueous fluoride solution are thus explained.

20.9.2. Chlorine: Electrolysis of fused NaCl produces chlorine at the anode. Electrolysis of a strong aqueous solution of NaCl also gives chlorine at the anode.

Note that the E° value of the chlorine/chloride couple is significantly lower than that of the fluorine/fluoride couple. Hence chlorine liberation can be achieved even by the electrolysis of aqueous chloride solution. However electrolysis of aqueous NaCl may give different products under different reaction conditions. The main reaction of electrolysis of aqueous NaCl may be expressed as:

$$2NaCl + 2H_2O \xrightarrow{\text{electrolysis}} \underset{\text{(anode)}}{Cl_2} + 2NaOH + \underset{\text{(cathode)}}{H_2}$$

If the purpose of the electrolysis is to recover all the products then the cell is so constructed that the anode and the cathode compartments are separated such that the chlorine cannot react with the NaOH produced at the cathode. On the other hand the same electrolysis may be carried out in a non-divided cell so that chlorine and NaOH react to give NaOCl in the cold, and sodium chlorate at a higher temperature (~75°C). (Also see section 20.7.2).

20.9.3. Bromine and Iodine: Bromine and iodine can be had by the above electrolytic procedures but for these halogens chemical oxidation methods are more convenient.

Chemical Oxidation Methods: These methods are based on oxidising the halides with appropriate oxidising agent. The following E° values of some couples are important to ascertain which of the oxidants can oxidise which halides:

oxidising strength increases ↑

$$\begin{aligned}
F_2 + 2e &\rightleftharpoons 2F^- &&; E^\circ = +\ 2.65 \text{ volts}\\
HClO + H^+ + e &\rightleftharpoons \tfrac{1}{2}Cl_2 + H_2O &&; E^\circ = +\ 1.63 \text{ volts}\\
MnO_4^- + 8H^+ + 5e &\rightleftharpoons Mn^{2+} + 4H_2O &&; E^\circ = +\ 1.52 \text{ ,,}\\
PbO_2 + 4H^+ + 2e &\rightleftharpoons Pb^{2+} + 2H_2O &&; E^\circ = +\ 1.45 \text{ ,,}\\
Cr_2O_7^{2-} + 14H^+ + 6e &\rightleftharpoons 2Cr^{3+} + 7H_2O &&; E^\circ = +\ 1.35 \text{ ,,}\\
Cl_2 + 2e &\rightleftharpoons 2Cl^- &&; E^\circ = +\ 1.36 \text{ ,,}\\
MnO_2 + 4H^+ + 2e &\rightleftharpoons Mn^{2+} + 2H_2O &&; E^\circ = +\ 1.23 \text{ ,,}\\
Br_2 + 2e &\rightleftharpoons 2Br^- &&; E^\circ = +\ 1.07 \text{ ,,}\\
Fe^{3+} + e &\rightleftharpoons Fe^{2+} &&; E^\circ = +\ 0.77 \text{ ,,}\\
I_2 + 2e &\rightleftharpoons 2I^- &&; E^\circ = +\ 0.54 \text{ ,,}
\end{aligned}$$

reducing strength increases ↓

Recall the rule that the oxidant of a redox couple can oxidise the reductant of another couple which has a lower E° value (Chapter 7). This rule and the above E° data show that no chemical oxidising agent in the above list can oxidise F^- to F_2. Oxidants with E° values of their couples above + 1.36 volts can oxidise Cl^- to Cl_2. Such oxidants are F_2, HClO, MnO_4^- and PbO_2. All oxidants with E° higher than 1.07 volts will oxidise Br^- to Br_2 (F_2, HClO, MnO_4^-, PbO_2, $Cr_2O_7^{2-}$, Cl_2, MnO_2) and all oxidants with E° values higher than 0.54 volts will oxidise I^- to I_2. In this context there is an interesting anomaly. It would appear that MnO_2 in acid medium would not oxidise Cl^- to Cl_2. Recall that the E° values refer to standard concentrations (1*M*). Now if we raise the concentration of H^+ ion (by adding enough acid) beyond 1*M* then the formal potential of $MnO_2/\ Mn^{2+}$ will tend to increase beyond + 1.23 volts. Also if we reduce the pressure of Cl_2 gas below 1 atomosphere by keeping the reaction mixture boiling the E° value of the chlorine/chloride couple will fall below 1.36 volts. Thus in practice MnO_2 in acid solution can oxidise chloride to chlorine. Some of the useful synthetic reactions are:

$$2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{2+} + 8H_2O + 5Cl_2$$

$$MnO_2 + 4H^+ + 2Cl^- \rightarrow Mn^{2+} + 2H_2O + Cl_2$$

In the laboratory chlorine is usually prepared by covering MnO_2 or $KMnO_4$ with concentrated HCl and gently warming the mixture.

$$3Br_2 + 6NaOH \rightarrow NaBrO_3 + 5NaBr + 3H_2O$$

The solution is acidified and the bromine collected:

$$NaBrO_3 + 5NaBr + 6HCl \rightarrow 3Br_2 + 3H_2O + 6NaCl$$

Iodine is extracted from two major sources: (*a*) from Chilean saltpetre and (*b*) from sea weed. (*a*) Chilean saltpetre ($NaNO_3$) contains some sodium iodate ($NaIO_3$). When the salt is recrystallised from water more soluble sodium iodate is retained in the mother liquor. The mother liquor is treated with sodium bisulphite when iodine is precipitated. The iodine is separated and purified by sublimation:

$$2NaIO_3 + 5NaHSO_3 \rightarrow I_2 + 3NaHSO_4 + 2Na_2SO_4 + H_2O$$

(*b*) Sea weeds are collected, dried and burnt. The ash contains about 1% alkali halide. The ash is treated with water and the soluble iodides separated from other insoluble materials. The solution is concentrated to crystallise other less soluble salts. The final filtrate is distilled with H_2SO_4 and MnO_2 in cast iron retorts:

$$2NaI + 3H_2SO_4 + MnO_2 \rightarrow 2NaHSO_4 + MnSO_4 + H_2O + I_2$$

The iodine is collected in stoneware receivers called *aludels*.

20.10. USES OF THE GROUP VIIB ELEMENTS

Chlorine is extensively used as a bleaching agent for wood pulp and paper, and cotton cloth (but not for wool and silk). It is also used in the manufacture of NaOCl, $CaOCl_2$, organic dyes, drugs, explosives etc.

Bromine is used in the manufacture of ethylene dibromide which is used in the synthesis of the 'antiknock' compound lead tetraethyl. It is also used in the manufacture of dyes and drugs.

Iodine is mainly used as an antiseptic. A solution of iodine in alcohol is known as *tincture of iodine*. It has also some use in the syntheses of drugs and dyes.

20.11. ANALYTICAL REACTIONS OF THE GROUP VIIB ELEMENTS

The redox potentials of the $X_2/2X^-$ couples vary widely in the series of the halogens. This variation has its effects on the reaction of the metal halides with concentrated H_2SO_4. Metal fluorides and chlorides liberate halogen hydracids whereas metal bromide and metal iodide give respectively bromine and iodine. The HF can be detected by etching of glass when it reacts with SiO_2:

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O \ ; \ SiF_4 + 2HF \rightarrow H_2SiF_6$$

HCl can be oxidised by MnO_2 to greenish yellow chlorine. Alternatively the chloride, under test, may be mixed with $K_2Cr_2O_7$ and concentrated H_2SO_4 and heated when red coloured CrO_2Cl_2 gas is evolved. The gas is absorbed in alkali and the chromate thus produced is tested as lead chromate. The chromyl chloride test is based on the formation of HCl from the chloride and hence the test responds only for ionic chlorides:

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$$

$$4HCl + K_2Cr_2O_7 + H_2SO_4 \rightarrow 2CrO_2Cl_2 + K_2SO_4 + 3H_2O$$

It fails for covalent chlorides like $HgCl_2$, Hg_2Cl_2 (see also Chapter 26).

The HBr and HI liberated in the initial stage of H_2SO_4 treatment of bromides and iodides are readily oxidised by hot and concentrated H_2SO_4:

$$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$$

$$2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$$

$$6HI + H_2SO_4 \rightarrow 3I_2 + S + 4H_2O$$

$$8HI + H_2SO_4 \rightarrow 4I_2 + H_2S + 4H_2O$$

The abobe reactions are also notable for the greater reducing power of I^-.

For quantitative estimation fluoride is precipitated as CaF_2 and weighed. Other halides are precipitated as silver halides in presence of dilute HNO_3 and weighed. Alternatively these latter halides may be determined volumetrically by titration against a standard silver nitrate solution using K_2CrO_4 as an indicator.

STUDY QUESTIONS

1. Compare group IA and group VIIB from the following points: (*a*) electronic configuration (*b*) position in the Periodic Table (*c*) ionisation potential (*d*) electron affinity and (*e*) standard potential.

2. Explain why the ionic radius of chloride ion is greater than the mean of the radii of fluoride and bromide ions while that of bromide ion is less than the mean of the radii of the chloride and iodide ions.

3. Chlorine has a higher boiling point than fluorine but ThF_4 has a higher boiling point than $ThCl_4$. Comment.

4. Why is it that fluorine brings about the highest coordination number of elements?

5. The oxidising power of the halogens decreases from fluorine to iodine but the reducing power of the halides increases from fluoride to iodide. Explain from the view point of standard electrode potentials. Cite reactions supporting the statement.

6. What reactions take place in the following cases: (*a*) Cl_2 is passed into a solution of NaBr, (*b*) I_2 is added to a solution of KCl, (*c*) Br_2 is added to a solution of KI.

7. Discuss on a comparative basis the chemistry of the halogen hydracids.

8. Give an account of the oxides and oxyacids of chlorine.

9. Fluorine cannot expand its octet but iodine can. Explain and support the statement from structural discussion of some compounds.

10. Are the chlorine and iodine molecules polar? What experimental evidences are needed in support of your answer? How would ICl behave?

11. Discuss Fajans' rules and cite supporting examples from binary halides.

12. Give a short account of (*a*) polyhalides and (*b*) interhalogens. Why is it that iodine forms most of these compounds?

13. How do you account for the decrease in acidity of the halogen oxyacids in the order $HOCl > HOBr > HOI$?

14. Perchloric acid has the formula $HClO_4$ whereas periodic acid is H_5IO_6. Explain. Cite some examples where periodate has stabilised higher oxidation states of metals.

15. Which of the four halogens is likely to be the most basic? Discuss some evidences in support of the predicted basic character.

16. Give an account of the basic properties of bromine and iodine. Is it true that in a given group basic properties always increase with increasing atomic number?

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21

Group O. The Noble Gases

21.1. DISCOVERY OF THE NOBLE GASES

Precision measurements and a trained mind often lead to great discoveries. The noble gases provide an example of such a class of discoveries. Cavendish in 1785 did some valuable probing into the composition of atmospheric air. He sparked atmospheric air in presence of excess oxygen and absorbed the N_2O_5 formed in water (giving HNO_3), and the excess oxygen in suitable absorbents. Amazingly he noted that there was a very small volume of a gas in the atmosphere that refused to combine with oxygen, and the volume of this gas was close to 1/120th of the original volume of air. This fine experiment went unnoticed for one full century till Rayleigh and Ramsay (1894) got interested in the problem from another viewpoint. In their interest in obtaining precision data on the density of nitrogen they selected two sources of nitrogen: one being atmospheric nitrogen (after removal of the oxygen from atmospheric air) and the other being decomposition of ammonium nitrite. ($NH_4NO_2 \rightarrow N_2 + 2H_2O$). They found out that nitrogen from ammonium nitrite weighed 1.2505 gm per litre whereas atmospheric nitrogen weighed 1.2572 gm. per litre. To scientists of ordinary run this difference in the third decimal point would not have meant much but the trained minds of Rayleigh and Ramsay could smell a connection between Cavendish's experiment and their own density measurements. They realised that the atmosphere must be carrying a new gaseous element or a mixture of new gaseous elements whose average density must be higher than that of nitrogen. Soon the oxygen of the atmospheric air was removed by means of red-hot copper, and then nitrogen by heated magnesium. The residual gas, of the same order of volume as in Cavendish experiment, was subjected to spectroscopic analysis and a new characteristic spectrum was obtained. The new element was named argon (meaning inert). Ramsay then set about examining the gas from the mineral cleivite, suspecting the gas to be argon. The gas was found to be inert but gave a characteristic yellow spectrum which was different from that of argon but identical with that of the sun's chromosphere. The gas was named helium which was also later identified by Rutherford in radioactive decay (Chapter 12). Ramsay then conjectured that helium and argon must belong to a new family of elements (group O) in the Periodic Table after group VIII, and that there must be another element in that group in between helium and argon. Fortunately at about this time liquefaction of air has been effected and Ramsay rightly turned to fractional distillation of liquid air for collection of argon and any other gas that might be present in air. A fraction from distillation of liquid air was collected, which had the composition of 60% argon plus other higher boiling rare gases, 30% oxygen and 10% nitrogen. The oxygen was removed by union with hydrogen, and the nitrogen by heated magnesium. The remaining rare gases were then liquefied and refractionated. Krypton and xenon were identified in different fractions by spectroscopic analyses. Helium and neon being comparatively low boiling were retained in the lighter fractions. The boiling points given below provide a comparative study:

Element	N_2	O_2	He	Ne	Ar	Kr	Xe	Rn
Boiling Point (°C)	−196	−183	−269	−246	−187	−152	−109	−62

The rare gases can also be fractionated effectively by their preferential adsorption on charcoal at preferred temperatures. At — 180°C charcoal adsorbs argon, krypton, xenon and radon, and on warming the charcoal to −80°C almost pure argon is obtained. After adsorption of argon and the heavier rare gases, the lighter ones neon and helium are adsorbed at −225°C on charcoal. Neon is more easily adsorbed than helium. Thus desorption at slightly above −225°C gives almost pure neon.

Radon is formed by the alpha emission of radium:

$$^{226}_{88}\mathrm{Ra} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{222}_{86}\mathrm{Rn}$$

It is a member of all the three natural radioactive disintegration series (page 300-302; Part I). Radon −222 is the longest-lived isotope of radon and has a half life of 3.82 days.

Note the composition of the rare gases of the air: 934 ml. of argon, 1.82 ml. of neon, 0.52 ml. of helium, 0.114 ml. of krypton and 0.009 ml. of xenon per hundred litres. Interestingly the total volume of the rare gases comes close to 1/120th of the volume of air—thus corroborating the Cavendish experiment of 1785! The discovery of the rare gases has been hailed as a triumph of a decimal point. Ramsay, who extended the horizon of the chemical elements by such commendable experimental efforts, was honoured by Nobel award in 1904.

21.2. GENERAL CONSIDERATIONS OF THE NOBLE GASES

Prior to 1960 helium, neon, argon, krypton, xenon and radon were known as inert or rare gases. Now these are called noble gases. The noble gases were not known at Mendeleev's time. When these elements were discovered and characterised, an extreme inertness marked these elements as distinct from any other element of the Periodic Table.

All the members of this family, excepting helium, have an s^2p^6 outer quantum shell composition (Table 21.1). Helium has a closed $1s^2$ configuration. The outer

s^2p^6 configuration of the other noble gases appears extremely stable. Based on the eight-electron outer shell of Ne, Ar, Kr, Xe and Rn one would guess their inclusion in group VIII of the Table. But Mendeleev had already allotted this group to the transition metal triads. Hence these elements along with He were included in a new group symbolised as group 'O'. The group 'O' adequately reflected the extreme inactivity of the noble gases.

The ionisation potentials are high (Table 21.1) but they do decrease down the group. The trend of the ionisation potentials indicates that if the elements show any reactivity at all it should be found in later elements only. Indeed since 1962 several compounds of xenon and to a lesser extent of krypton have been synthesised. Radon being a rare radioactive element has not been studied to the same extent as xenon and krypton. The electron affinities of these elements must be very poor since no noble gas anions are known.

The extreme inertness of these elements is reflected in their monatomic nature. That these noble gases are all monatomic have been verified from a study of their specific heats at constant pressure (C_p), and at constant volume (C_v). For monatomic gases the atoms have no vibrational energy (as might be the case for polyaiomic molecules) and hence their molar heat capacities do not involve any internal contributions. The values of C_p and C_v should therefore correspond to those for ideal gases. The ratio C_p/C_v ($C_p = \frac{5}{2}R$ and $C_v = \frac{3}{2}R$ where R is the gas constant) is $\frac{5}{3}$, that is, 1.666 for such gases. The noble gases have their C_p/C_v ratios close to 1.666. For diatomic molecules internal vibrations are possible, and these will contribute to the specific heats so that C_p, C_v and C_p/C_v are different from those of the monatomic noble gases. For example ihe Cp/Cv ratios for H_2, O_2, N_2, NO etc. are in the range 1.40–1.41. According to valence bond concept diatomic noble gas-molecules (such as He_2, Ne_2, etc.) are not formed because the atoms of these elements do not possess any unpaired electron. On molecular orbital model for He_2 we have to place two electrons in the bonding 1s orbital and two electrons in the antibonding 1s* orbital so that there is no net gain in stability. (cf: Fig. 21.1). According to Mulliken's M.O. theory bond order of He_2 is:

Bond Order =

$$\frac{\begin{pmatrix}\text{number of electrons}\\ \text{in bonding M.O.}\end{pmatrix} - \begin{pmatrix}\text{number of electrons}\\ \text{in antibonding M.O.}\end{pmatrix}}{2}$$

$$= \frac{2-2}{2} = 0$$

Thus diatomic helium does not exist.

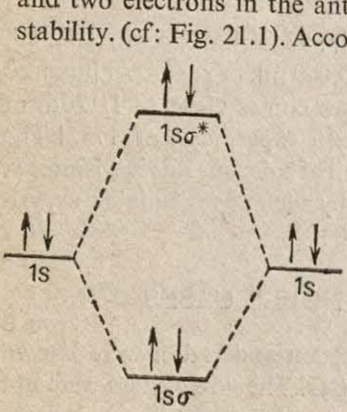


Fig. 21.1. M. O. diagram of He_2

The only interaction in the monatomic noble gases is the weak van der Waals' force. The van der Waals' forces in noble gases are far weaker than the van der Waals' forces in compounds having comparable molecular weights but less symmetrical electron distributions. The latter types of compounds have significantly higher electrostatic and polarisation interactions. The van der Waals' forces responsible for liquefaction of the noble gases are of the *instantaneous dipoles interaction* type (Chapter 5).

Table 21.1. Electronic Configurations and Some Properties of Group 'O' Elements

Element	Atomic Number	Electronic Configuration	Ionisation Potential (*ev*)	van der Waals' radii (A)
Helium	2	$1s^2$	24.58	1.2
Neon	10	$[He]2s^22p^6$	21.56	1.6
Argon	18	$[Ne]3s^23p^6$	15.75	1.9
Krypton	36	$[Ar]3d^{10}4s^24p^6$	13.99	2.0
Xenon	54	$[Kr]4d^{10}5s^25p^6$	12.13	2.2
Radon	86	$[Xe]4f^{14}5d^{10}6s^26p^6$	10.75	—

21.3. COMPOUNDS OF THE NOBLE GASES

Chemists have given the noble gases a far too respectful treatment for too long a time. From time to time, however, some experiments had been undertaken to test the ability of the noble gases to form compounds. These unrewarding studies included interactions of the noble gases with the electron-deficient boron halides and boron trimethyl, and interaction of argon, krypton and xenon with phenol giving clathrates. These studies at best indicated some sort of very loose adduct formation. These adducts could not be regarded as definite chemical entities.

In the beginning of the last decade Bartlett achieved a breakthrough in this area. Bartlett, while working on the oxidising properties of the gas PtF_6, observed that with molecular oxygen a crystalline product $O_2^+[PtF_6]^-$ was obtained. The PtF_6 oxidised O_2 to O_2^+ cation. Bartlett immediately recognised that similar experiments with some of the noble gases, particularly with xenon, might be rewarding since both O_2 and Xe had similar ionisation potentials (O_2, 12.2 *ev*; Xe, 12. 13 *ev*). The deep red PtF_6 vapour was allowed to mix with an equal volume of xenon at the same pressure whereby an orange yellow solid $Xe[PtF_6]$, insoluble in CCl_4 and with a small vapour pressure, was obtained. After this breakthrough several laboratories got actively interested in compounds of the noble gases and more than a hundred papers appeared within a few years. Most compounds have been obtained with xenon and a few with krypton (Table 21.2). The compounds are fluorides, oxide fluorides and oxides of xenon and krypton.

21.3.1. Syntheses: The different *synthetic approaches* can be summarised under the following heads:

1. *Thermal process using high temperature and pressure, and excess of fluorine:* For XeF_4 one part xenon and five parts fluorine were mixed under pressure in a nickel vessel and heated to 400°C for one hour and then rapidly cooled to room temperature. The nickel crucible was weighed before and after the introduction

Table 21.2. Some Typical Compounds of Xenon and Krypton

Compound Types	Xenon	M.P. (°C)	Krypton
Fluorides	XeF_2 (colourless crystals)	129	KrF_2 (volatile colourless solid)
	XeF_4 (,,)	117	
	XeF_6 (,,)	49.6	KrF_4
	$XePtF_6$ (red solid)		
	$XeF_2 \cdot 2SbF_5$ (Yellow solid)		
Oxide fluorides	$XeOF_4$ (colourless liquid)		
	XeO_2F_2		
Oxides and Oxyacids	XeO_3 (colourless crystals)		H_2KrO_4
	XeO_4 (colourless gas)		
	Na_4XeO_6 (colourless solid)		

of the gases. It was also weighed after pumping off the unreacted fluorine at the end of the experiment. Thus the interacting ratios of fluorine to xenon in different runs were found to be 4.05, 3.92, 3.91, 3.97 etc. XeF_6 was obtained by heating xenon (1 part) and fluorine (4 to 20 parts) to 300–700°C at 200 atmospheres pressure in nickel or stainless steel vessels.

2. *High voltage electric discharge:* XeF_4 has been obtained from 2 parts fluorine and 1 part xenon by this method. Altering the ratio to 1 : 1 gave XeF_2. The discharge was passed by means of an induction coil and varied from 1100 volts and 31 mA to 2800 volts and 15 mA.

3. *High voltage discharge through xenon and CF_4:* The principal compound synthesised by this method is XeF_2.

4. *Conversion of a fluoride to an oxide fluoride and to an oxide by heating in a quartz vessel:* XeF_6 is sealed in a quartz vessel and heated to ~ 50°C when the following reaction occurs:

$$2XeF_6 + SiO_2 \rightarrow 2XeOF_4 + SiF_4$$

The vessel is cooled to −78°C, SiF_4 pumped off and the colourless $XeOF_4$ collected. If the above reaction is allowed to run for a prolonged period the reaction with silica is complete and an oxide is obtained:

$$2XeOF_4 + SiO_2 \rightarrow 2XeO_2F_2 + SiF_4$$

$$2XeO_2F_2 + SiO_2 \rightarrow 2XeO_3 + SiF_4$$

5. *Hydrolysis of a fluoride to an oxide or oxyacid:* The oxide is also formed as a result of the acid hydrolysis of XeF_4 or as a result of slow hydrolysis of XeF_6 with water vapour. Xenic acid, perxenic acid, xenates and perxenates are formed in solution during acid, neutral or alkaline hydrolysis of XeF_4 or XeF_6. XeF_6 when hydrolysed by 2.5*M* NaOH precipitates *sodium perxenate:*

$$2XeF_6 + 16NaOH \rightarrow Na_4XeO_6 + Xe + O_2 + 12NaF + 8H_2O$$

Sodium perxenate can be precipitated in pure form and in better yield by passing ozone into a solution of XeO_3 in 1*M* NaOH. The salt is a white crystalline material $Na_4XeO_6.xH_2O$ ($x \sim 0$ to 8 depending on the mode of drying). On drying over magnesium perchlorate in vacuo x is 0.5. Sodium perxenate is very stable and can be stored indefinitely at room temperature. This is a very powerful oxidant. The redox potential of the couple XeO_6^{4-}/XeO_3 is ~ 3.0 volts in acid solution. It can oxidise manganese (II) instantly to permanganate without the use of any catalyst:

$$5XeO_6^{4-} + 2Mn^{2+} + 14H^+ \rightarrow 2MnO_4^- + 5XeO_3 + 7H_2O$$

21.3.2. Bonding: The bonding in noble gas compounds has generated much debate. It is gratifying to note that there is no need to modify our bonding theories to cover these compounds.

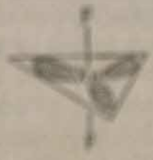
Valence Bond Approach: The xenon fluorides have an inherent connection with the polyhalide ions. Thus in XeF_2 and in ICl_2^- both xenon and iodine have a valence shell of ten electrons. The five electron pairs in XeF_2 or ICl_2^- will assume a trigonal bipyramidal arrangement (sp^3d hybridisation of Xe or I).

$$\mathrm{Xe}\ \underset{5s}{\underline{\uparrow\downarrow}}\ \underset{5p}{\underline{\uparrow\downarrow}}\ \underset{5p}{\underline{\uparrow\downarrow}}\ \underset{5p}{\underline{\uparrow\downarrow}}\ \underset{5d}{\underline{\quad}}\ \text{hybridises to}\ \underset{5(sp^3d)}{\underline{\uparrow\downarrow}}\ \underset{5(sp^3d)}{\underline{\uparrow\downarrow}}\ \underset{5(sp^3d)}{\underline{\uparrow\downarrow}}\ \underset{5(sp^3d)}{\underline{\uparrow}}\ \underset{5(sp^3d)}{\underline{\uparrow}}$$

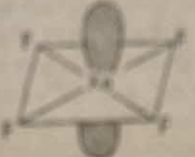
The two sp^3d orbitals with one electron overlap with fluorine orbitals with unpaired electrons. The other three hybrid orbitals carry the lone pairs. According to VSEPR theory the three lone pairs occupy equatorial sites and the two fluorine apical sites (21-I). The F—Xe—F bond angle thus becomes ~ 180°. In XeF_4 and in ICl_4^- both Xe and I have a valence shell of twelve electrons, and therefore the electron pairs are arranged in an octahedral geometry (sp^3d^2 hybridisation).

$$\mathrm{Xe}\ \underset{5s}{\underline{\uparrow\downarrow}}\ \underset{5p}{\underline{\uparrow\downarrow}}\ \underset{5p}{\underline{\uparrow\downarrow}}\ \underset{5p}{\underline{\uparrow\downarrow}}\ \underset{5d}{\underline{\quad}}\ \underset{5d}{\underline{\quad}}\ \text{hybridises to}\ \underset{5(sp^3d^2)}{\underline{\uparrow\downarrow}}\ \underset{5(sp^3d^2)}{\underline{\uparrow\downarrow}}\ \underset{5(sp^3d^2)}{\underline{\uparrow}}\ \underset{5(sp^3d^2)}{\underline{\uparrow}}\ \underset{5(sp^3d^2)}{\underline{\uparrow}}\ \underset{5(sp^3d^2)}{\underline{\uparrow}}$$

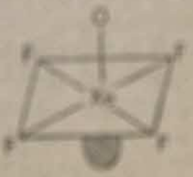
The four hybrid orbitals with one electron on each then overlap with the fluorine orbitals also having unpaired electrons. There will be two lone pairs which will take the apical sites leaving the equatorial sites for the fluorine atoms. The XeF_4



(21-I)



(21-II)



(21-III)

molecule has therefore F—Xe—F bond angles of 90°, the xenon and the fluorine atoms being in a square plane (21-II). In $XeOF_4$ we assume a double bond between xenon and oxygen, and single bonds between xenon and fluorine. Then xenon electrons may be assumed to be distributed as under:

⥮	↑	↑	↑	↑	↑	↑
$5(sp^3d^2)$	$5(sp^3d^2)$	$5(sp^3d^2)$	$5(sp^3d^2)$	$5(sp^3d^2)$	$5(sp^3d^2)$	$5d$

Five unpaired electrons in the five sp^3d hybrid orbitals make five sigma bonds with the four fluorine and the oxygen. The sixth unpaired electron in a suitable *d*-orbital of xenon then overlaps with a *p*-orbital of oxygen to make the π-bond, thus completing the double bond between xenon and oxygen. The four fluorine atoms occupy equatorial sites, the oxygen one apical site and the other apical site being taken up by the lone pair (21-III).

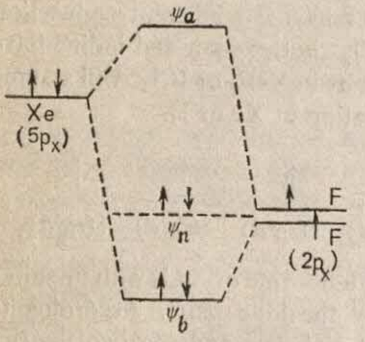


Fig. 21.2. Molecular orbitals of FeF_2

Molecular Orbital Approach: The outer electronic configuration of Xe is $(5s)^2$ $(5p_x)^2$ $(5p_y)^2$ $(5p_z)^2$ and that of fluorine, we take, as $(2s)^2$ $(2p_x)^1$ $(2p_y)^2$ $(2p_z)^2$. Taking x axis as the bond axis of linear XeF_2 we consider an interaction among the $5p_x$ orbital of Xe and the two $2p_x$ orbitals of the two fluorine atoms. The three A.O.'s will combine to produce three M.O.'s—one bonding, one non-bonding and the other antibonding. The four electrons of the three A.O.'s are distributed as two electron pairs in the bonding and non-bonding orbitals (Fig. 21.2). For XeF_4 we assume M.O. formation between $5p_x$ orbital of Xe and two $2p_x$ orbitals of two F's along x axis, and between $5p_y$ orbital of Xe and two $2p_y$ orbitals of two F's along y axis. In XeF_2 three electron pairs will be left on Xe: $(5s)^2$ $(5p_y)^2$ $(5p_z)^2$ while in XeF_4 there will be two electron pairs on Xe: $(5s)^2$ $(5p_z)^2$. Such M.O. scheme can also be envisaged for XeF_6.

21.4. USES OF THE NOBLE GASES

1. *Neon* is a non-conductor of electricity. But it starts conducting under low pressure (10—20 mm) and under high voltage (~ 200 volts). Under these conditions ionisation of neon occurs. The excited ion while returning to its ground state emits a characteristic red light. This principle is made use of in the neon conduction lamps known as neon sign tubes. The current consumption is very small so that such neon tubes, so popular for advertisement, become economically viable. By the addition of other noble gases or of mercury vapour or by choosing coloured glass many different shades of colour can be produced. Neon tubes respond immediately to putting 'on' and 'off' of the connecting switch.

2. Argon, by far the plentiest of the noble gases, is mainly used to protect metal surfaces from oxidation during arc welding of steel, aluminium and magnesium. Another very important use of the gas is to be found in common incandes-

cent filament bulbs. In order to prolong the life of the tungsten filament from vaporisation and oxidation the filament lamps are filled with argon. An evacuated bulb slowly allows vaporisation of the hot tungsten filament producing a fine soot on the inside surface of the bulb. To obviate this the inside of the bulb used to be filled up by inert nitrogen. However in presence of nitrogen slow formation of tungsten nitride occurred. Nitrogen is therefore replaced by argon which is superior because (*a*) its thermal conductivity is lower than that of nitrogen (the filament is better protected against heat loss) and (*b*) it is more inert than nitrogen.

3. Nitrogen is soluble in blood under pressure. When divers and tunnel workers (who have to expose themselves to high pressures) come suddenly to normal pressure then the dissolved nitrogen (from inhaled air) is abruptly released as small bubbles in the blood stream. This causes severe pain. For this reason helium-oxygen mixture (helium as a diluent) rather than ordinary air is provided to such workers. Helium is not soluble in blood stream.

4. In varied scientific experimentation special inert atmosphere needs to be maintained. For such purposes helium and argon are used. For low temperature in the region of a few degrees Kelvin liquid helium finds extensive use.

STUDY QUESTIONS

1. Discuss the electronic configurations, position in the Periodic Table and the consequent propetries of the noble gases.

2. How do you account for the fact that xenon forms most of the compounds and not neon?

3. Discuss the syntheses and bonding of the noble gas compounds.

4. Give an account of the applications of the noble gases.

5. Explain monatomic character of helium on valence bond and molecular orbital theories.

6. "The discovery of the noble gases has been hailed as triumph of a decimal point." Elaborate the statement.

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22

A General Survey of the Transition Elements

22.1. INTRODUCTION

Much of the modern inorganic chemistry is really transition metal chemistry. The entire area of coordination chemistry virtually hangs around transition metals. We have already defined a transition element as one that has an incompletely filled *d* or *f* subshell in its elementary or ionic state. This definition allows inclusion of the coinage metals such as copper, silver and gold within the transition family. Copper in its elementary state has a filled $3d^{10}$ subshell but in copper (II) state it has an incomplete $3d^9$ subshell (Chapter 1). The definition, however, excludes zinc since the element has a filled $3d^{10}$ subshell both in the elementary state and in the bivalent state:

Copper	(29)	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$3d^{10}$	$4s^1$
Zinc	(30)	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$3d^{10}$	$4s^2$

Recalling from Chapter 2 we have the following spread of the transition element in the Periodic Table:

First series of transition elements: Sc(21) to Cu(29).

Second series of transition elements: Y(39) to Ag(47).

Third series of transition elements: Hf(72 to Au(79).

First series of inner transition elements: La(57) io Lu (71).

Second series of inner transition elements: Ac(89) io Lw(103).

We thus have a total of fifty six transition elements out of 103 elements.

These transition elements can be regrouped under *d*-block and *f*-block elements. The inner transition series (*f*-block elements) include the lanthanides and actinides—a total of 30 elements. The remaining 26 elements form the three series of *d*-block transition elements. We discuss below some general features of the *d*-block transition elements showing that most of their properties originate from their incomplete *d*-orbitals.

22.2. GENERAL FEATURES OF THE *d*-BLOCK TRANSITION SERIES ELEMENTS

The first (*d*-block) ttansition series elements and also the second and the third series have the following general features:

8. Atomic and ionic radii change very slowly along a particular series.

2. Ionisation potentials and electronegativities change very slowly along a particular series.

3. The elements give rise to several valence states.

4. Their chemistry is dominated by complex formation.

5. They often give rise to coloured compounds.

6. They often give paramagnetic compounds.

7. They are generally high melting and high boiling metals.

8. Some of these elements and their compounds serve as effective catalysts.

All these general features arise out of the incompletely filled *d*-orbitals. The 3*d*- and the 4*s*-orbitals lie very close to each other and in multielectron system the 4*s*-orbital lies a little lower than the 3*d*-orbital (Fig. 1.21, Chapter 1). However a reversal of the relative order of the 3*d* and 4*s* occurs when the 3*d* orbitals have been fed with some electrons. This can be understood from the radial distribution curves of the 3*d* and 4*s* orbitals (Fig. 22.1). Of the 3*d* and 4*s* orbitals, the 4*s* orbital has (4—1) i.e. 3 small concentric spheres underneath the main 4*s* shell (Chapter 1 and Appendix), although these inner spheres carry only a small probability of finding the electron. Also note that the 4*s* shell spreads out into space more than the 3*d* does. We arrive at an important conclusion that the 4*s* orbital is far more penetrating than the 3*d* orbital. Because of this the 4*s* shell sees more of the positive nuclear charge than does the 3*d* shell. This makes the energy of the 4*s* orbital fall and thus makes it more stable than the 3*d* orbital. Hence in potassium and calcium the 4*s* shell is occupied in preference to the 3*d* orbitals. After calcium the 3*d* orbitals are being filled till we reach copper. Since the 4*s* orbital sees more of the nuclear charge it can screen (shield) the nuclear charge more effectively than is possible by a 3*d* electron. Remembering therefore that the 3*d* orbitals are not as much penetrating (that is lower screening capacity) as the 4*s* orbital it so happens that with increasing atomic number in Sc, Ti, etc the effective nuclear charge increases rapidly. After the addition of a few 3*d* electrons the energy of the 3*d* orbitals now rapidly falls below the 4*s* level because of increasing effective nuclear charge felt by the 3*d*-electrons.

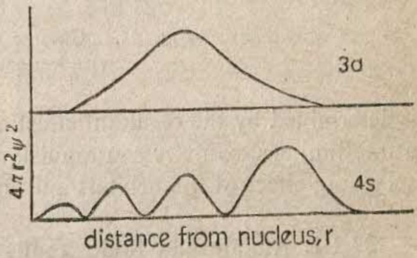

Fig. 22.1. Radial distribution function of the 3*d* and 4*s* orbitals (schematic)

Thus to begin with the 4*s* orbital has lower energy than the 3*d*. But on the addition of some 3*d* electrons the energy of the 3*d* level becomes lower than the 4*s* electron (Fig. 22.2). Experiments demonstrate that during ionisation the first series transition elements lose first the 4*s* electron (compare Fig. 22.2) raiher than any of the 3*d* electrons. Thus in multi-electron systems the exact position

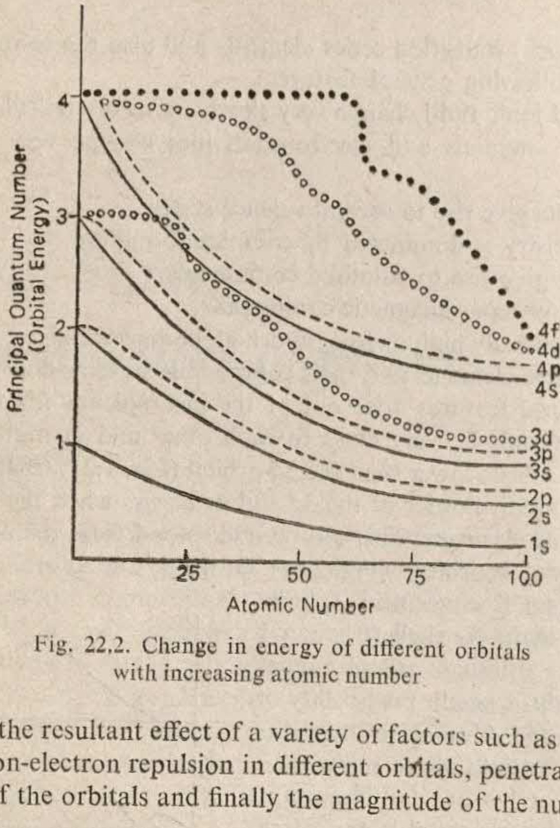

Fig. 22.2. Change in energy of different orbitals with increasing atomic number

is determined by the resultant effect of a variety of factors such as nucleus-electron attraction, electron-electron repulsion in different orbitals, penetration and mutual screening effect of the orbitals and finally the magnitude of the nuclear charge.

22.1.1. Atomic and Ionic Radii. For the first transition series electrons are added to the 3*d* orbitals, all of which have the same radial distribution. Such addition cannot add to the size of the atom; instead increasing nuclear charge brings about a slow contraction in size:

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Aiomic Radius (A)	1.47	1.34	1.27	1.26	1.26	1.26	1.25	1.28	1.38
Ionic (M^{2+}) Radius (A)	0.72	0.65	—	0.82	0.77	0.72	0.68	—	0.74

The ionic radii have been obtained by subtracting the ionic radius of oxide ion (1.40A) from the M—O distance found in bipositive metal oxides. Some slight irregularities in size have been ascribed to crystal field effects. The preferential occupancy of the t_{2g} (d_{xy}, d_{xz}, d_{yz}) orbitals or of the e_g $(\mathrm{d}_{x^2-y^2}, d_{z^2})$ orbitals (all of which are not of similar shape and orientation) by electrons is believed to be the cause of the above irregularities. Note that t_{2g} electrons repel ligands less strongly than e_g electrons. Hence a greater decrease in ionic radius occurs if the nuclear charge is increased by one with the placement of an electron in the t_{2g} level than in the e_g level. See also page 234, Part I.

22.2.2. Ionisation Potentials and Electronegativities. With a slow decrease in size and an increase in nuclear charge the ionisation potentials may be expected to show a slow increase along the series. The first ionisation potentials show a slow increasing trend but not in a graded manner. With an increase in the nuclear charge the electronegativities of the elements show a slow increasing trend:

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
First Ionisation Potential (*ev*)	6.82	6.74	6.76	7.43	7.90	7.86	7.63	7.72	7.39
Electronegativity (in common oxidation state)	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6

22.2.3. Variable Valence. A most remarkable feature of the transition elements is their ability to exhibit several valences. We have earlier mentioned that in multi-electron systems, particularly in the *d*-block transition series, the exact energy is determined by the resultant effect of many factors. For regular non-transition elements a group of electrons outside the noble gas core have essentially the same energy. Therefore if it is possible to use one electron for valence purpose it is possible to use the whole lot. That is, such elements will show one fixed valence. On the other hand in a transition element the energies of the *ns* and the first one or two $(n-1)d$ electrons are almost the same. But when more $(n-1)$ *d*-electrons are present their energies differ considerably among themselves and also from the *ns* electrons so that chemical reagents of different strengths can withdraw or utilise different number of electrons. Hence variable valence is a natural consequence in the transition elements. The energy required to withdraw more and more *d*-electrons is eventually compensated by energy released in the formation of suitable bonds. In high oxidation states it will be unreasonable to assume (because of increasing ionisation potential and electronegativity) that electrons are completely removed from the metal orbitals; instead they may be assumed to participate in covalent bonding with suitable negative or neutral groups (O^{2-}, Cl^-, IO_6^{5-}, dipyridyl, etc). Valence then reduces to formal oxidation number. Table 10.9 (Chapter 10) gives an idea of the many different oxidation states of the first transition series elements.

22.2.4. Complex Formation. A dominant feature of the transition metal chemistry is complex formation. Compare the following charge/radius ratios (ionic potentials) for some common elements (Table 22.1).

Note that the three regular non-transition elements have lower values for charge/radius ratios than the three transition elements. Smaller ionic radii coupled

Table 22.1. Charge/Radius Ratios of Some Elements

Ion	Charge	Radius (A)	Charge/Radius	Ion	Charge	Radius (A)	Charge/Radius
K^+	+1	1.33	0.76	Cu^+	+1	0.96	1.04
Rb^+	+1	1.48	0.68	Ag^+	+1	1.26	0.80
Cs^+	+1	1.69	0.59	Au^+	+1	1.37	0.73

with larger effective nuclear charge (due to smaller screening effect of the 3*d*-orbitals) exerts a greater attractive force on the donor atoms of ligands. This leads to complex formation. We can take an alternative view in terms of the crystal field. The different shapes of the *d*-orbitals and their different orientations in a crystal field (t_{2g}/e_g for octahedral field) give rise to extra stabilisation (CFSE) in several $3d^n$ ions due to preferential occupation of the lower t_{2g} orbitals (Chapter 10). Such extra stabilisation is clearly not possible for regular non-transition metal ions with filled *s* and *p* orbitals. *s* and *p* orbitals are not split in an octahedral or tetrahedral crystal field.

Complexes are of a diverse nature due to a wide range of variation in oxidation states, ligands, crystal field strength, coordination number, overall charge, etc. Low oxidation states are, in general, stabilised by electron deficient molecules having empty π-orbitals to receive back donated electrons. Such ligands are CO, NO, PR_3, dipyridyl, ethylene, etc. High oxidation states are stabilised by strong σ-donors eg: dipyridyl, o-phenanthroline, periodate, tellurate, diarsine, etc. (Chapter 10).

22.2.5. Coloured Compounds of Transition Elements. Transition metal complexes of the first, second and the third series admit of *d—d* transitions. Electrons from lower t_{2g} orbitals may be excited to higher e_g levels (for octahedral complexes) or from *e* level to higher t_2 level (for tetrahedral complexes). The energy gap in t_{2g}/e_g set or e/t_2 set being small, only small amount of energy is required to make the transition. This energy is absorbed from the surrounding light and the sample transmits the complementary colour (Fig. 22.3). The apparent colour of a substance or its solution is always the complement of the colour which is absorbed by the substance or its solution. Human eye can only follow the colour in the visible region of the electromagnetic radiation. Too high energy transitions or too low energy transitions cannot be distinguished by human eye. Electromagnetic radiation may be divided conveniently into three regions: visible range

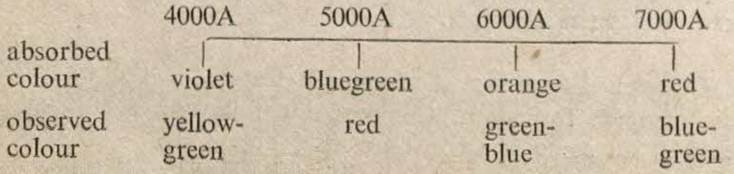

FIG. 22.3. A schematic representation of absorbed colour and observed colour

(4000A-8000A), ultraviolet range (below 4000A) and the infrared range (above 8000A). A compound which we find to be blue absorbs radiation in the red region, and transmits blue. Hydrated copper (II) sulphate is blue green because it absorbs light of wave length ~7500A (= 750 mμ*). A substance that absorbs in the blue region (4500A—4800A) will appear yellow or orange, and one that absorbs green (5000A—5600A) will appear purple. Table 22.2 will serve as further aid.

In addition to *d—d* transition or in the absence of *d—d* transition some metal complexes containing oxidisable/reducible metal ion and a ligand of opposite character may give rise to charge transfer transition in the ultraviolet. These transitions may have a tail in the visible which may be responsible for making the complex look coloured to human eye. For details see page 239-240, Part I.

Table 22.2. Colours of Visible Radiation

Colour absorbed	Approximate Wave Length (A) of the absorbed colour	Complementary colour observed
Violet	4000—4500	Yellow-green
Blue	4500—4800	Yellow
Green blue	4800—4900	Orange
Blue green	4900—5000	Red
Green	5000—5600	Purple
Yellow green	5600—5750	Violet
Yellow	5750—5900	Blue
Orange	5900—6250	Green blue
Red	6250—7500	Blue green

22.2.6. Paramagnetism of Transition Metal Compounds. Transition metal complexes are of enormous magnetochemical interest. In such compounds the number of *d*-electrons varies in different oxidation states. These *d*-electrons are perturbed to different extent due to complex formation. Strong donor ligands can force spin pairing. Stereochemistry, crystal field splitting, donor strength of the ligands, etc. ultimately decide the magnetic properties of the complexes. These have been discussed in Chapters 10 and 11. The following equation applies to the first transition series elements:

$$\mu = \sqrt{L(L+1)+4S(S+1)}\beta$$

where L, S and β have their usual significance. In general for the complexes of the first series transition elements L is 0 so that $\mu = \mu_{\text{spin only}} = \sqrt{4S(S+1)}\beta = \sqrt{n(n+2)}\beta$ where n is the number of unpaired electrons. For cobalt (II) complexes and nickel (II) complexes the magnetic moment values are substantially higher than the spin-only values (Table 10.3; Chapter 10).

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* 10A = 1 mμ (millimicron) = 1 nm (nanometre)

22.2.7. Catalytic Activity of Transition Metals. Transition metals are well known for their catalytic activities. Synthesis of ammonia makes use of iron–molybedenum catalyst, that of sulphuric acid needs V_2O_5 or spongy platinum and so on. The catalytic activity of the regular transition elements is undoubtedly due to the availability of the *d*-orbitals. The *d*-orbitals, being exposed to the surface, can participate in the formation of some *activated complex* which serves as intermediates in an overall chemical process. These intermediates produce reaction paths of lower activation energy for otherwise slow reactions and thus enhance the reaction rates. The inner transition elements having submerged *f*-orbitals are much less effective as catalysts.

22.3. SOME SPECIAL FEATURES OF THE SECOND AND THIRD TRANSITION SERIES ELEMENTS

All the above general features of the first transition series will apply to the elements of the second and third series transition elements. In addition a few more points may be noted.

As we move down a particular family of transition metals in a Periodic group there is an increase in size from the first to the second but the size increase from the second to the third is negligible (Table 22.3).

Table 22.3. Variations in Size of Transition Elements of Different Series

Transition Series	Element	Atomic Radius(A)	Ionic(M^{4+}) Radius(A)	Element	Atomic Radius(A)	Ionic(M^{+}) Radius(A)
First	Ti	1.47	0.68	Cu	1.28	0.96
Second	Zr	1.60	0.80	Ag	1.43	1.26
Third	Hf	1.59	0.81	Au	1.44	1.37

The 4*d* or the 5*d* orbitals of the later series are more spread out in space than the 3*d* orbitals. This leads to a smaller interelectronic repulsion since two electrons have now a bigger room to share. Reduced interelectronic repulsion plus increased nuclear charge lead to a closer approach of the ligand orbitals to the metal orbitals in complexes. This close approach results in a larger crystal field splitting which also favours spin pairing. In effect therefore spin pairing becomes easier in later transition series. For example, chloro complexes in the first transition series are all high spin but in the later series chloro complexes are low spin. $[NiCl_4]^{2-}$ is paramagnetic ($\sim$3.9 B.M.) but $[PdCl_4]^{2-}$ and $[PtCl_4]^{2-}$ are diamagnetic.

22.4. *d*-BLOCK TRANSITION ELEMENTS VERSUS NON-TRANSITION ELEMENTS

We enumerate some of the important distinctions between transition (*d*-block) and non-transition elements in Table 22.4.

Table 22.4. Comparison of *d*-block Transition Elements and Non-Transition Elements

Transition Elements	Non-transition elements
1. The elements or their ions have partly filled *d*-orbitals: (eg: Cr(III) ($3d^3$); Mn(II) ($3d^5$); Ni(II) ($3d^8$); Cu(II) ($3d^9$). Along a particular series of transition elements electrons are added to the penultimate *d*-orbitals.	1. These elements have no partly filled *d*-orbitals. Their inner shells have all filled *s*, *p* or *d* levels. Along a period of non-transition elements electrons are added to the outermost *s*- or *p*-orbitals, (eg: Na^+ ($3d^0$); Zn(II) $3d^{10}$)
2. Along a transition series there is a slow contraction in size with increasing atomic number. The ionisation potential and electronegativities increase but very slowly along a period with increasing atomic number. These changes are somewhat irregular.	2. Along a period there occurs a good deal of decrease in size. Ionisation potentials and electronegativities increase very decisively.
3. The outermost *s*- and the penultimate *d*-electrons can be disturbed by chemical reagents to different extent. Hence these elements show variable valences. (eg: Cu (+1, +2, +3); Mn (0 to +7); Fe(−2, −1, 0, +2, +3, +6); Ni(0, +1, +2, +3, +4) etc.	3. These elements usually show a definite fixed valence. Sometimes valences other than the group valence are exhibited. The variation is caused by a wide difference in the ionisation potential of the *s*- and *p*-electrons (inert pair effect). (eg: Sn (+2, +4): (Pb (+2, +4)
4. Their chemistry is dominated by complex formation. (eg: $[Cu(NH_3)_4]^{2+}$; $[Co(NH_3)_6]^{3+}$; $[NiCl_4]^{2-}$; $[Ni(CO)_4]$ etc.)	4. Complex formation is not an important feature of their chemistry.
5. Their compounds are mostly cocoloured. The colour is due to small energy transition of the *d*-electrons from t_{2g} to e_g level for octahedral complexes or from *e* to t_2 level for tetrahedral complexes. For yet other stereochemistries other transitions will be possible due to	5. Since *d*-electrons are not involved electron transitions may occur from *s*- or *p*-orbitals to the next higher *s*-orbital. This is a high energy transition requiring absorption of much energy so that the transmitted light falls in the infrared region. Some coloured com-

Transition Elements	Non-transition elements
further splitting of the *d*-orbitals. These *d–d* transitions occur in the visible region of the electromagnetic radiation. In some cases charge transfer transitions may be responsible for colour. Although such transitions occur generally in the ultraviolet region these may have a tail in the visible region, which may make the compounds appear coloured to the eye (page 240, Part I).	pounds such as Sb_2S_5, HgS, etc owe their colour to other factors (charge transfer transition). Such transitions occur when the cation or the anion (or the ligand) is either strongly reducing or oxidising while the other partner has the opposite character. Electron transfer can then occur from the reducing agent to the oxidising agent (page 240, Part I).
6. Many of their complexes are paramagnetic. Since more than one oxidation state is possible and since each of these states may form complexes there arises a wide scope of spin-free (high spin) and spin-paired (low-spin) complexes. (eg: high spin Fe(III) in $[FeF_6]^{3-}$ has $\mu \simeq 5.9$ B.M. while low spin Fe(III) in $[Fe(CN)_6]^{3-}$ has $\mu \simeq 1.73.$ B.M.	6. All their compounds are normally diamagnetic since no unfilled *s*, *p* or *d* subshells are involved. In rare cases paramagnetism arises due to odd number of electrons as in NO, NO_2, ClO_2, etc.

22.5. THE INNER TRANSITION SERIES ELEMENTS

These elements have a partly filled *f* subshell in their elementary or ionic state. Unlike the 3*d*-orbitals, the 4*f*-orbital is not the penultimate shell. For the lanthanides the *f*-orbital is the 4*f* subshell whereas the outer shell is 6*s*. These *f*-electrons being deeper seated behave as though they belong to the entire inner core, and are not readily affected by chemical reagents. The inner transition elements can be subdivided into two families: (1) Lanthanides (La 57 to Lu 71; family symbol, Ln) form the first series of inner transition elements: (2) Actinides (Ac 89 to Lw 103) form the second series of inner transition elements.

22.5.1. The Lanthanides. The lanthanide atoms and their trivalent ions have the following configurations:

Lanthanide atoms: [Pd] $4f^n5s^25p^65d^16s^2$ or [Pd] $4f^{n+1}\ 5s^25p^66s^2$

Lanthanide (M^{3+}) ions: [Pd]$4f^n5s^25p^6$

Once the three electrons are lost giving the M^{3+} ions the *f*-orbital electrons stay under an envelope of a stable $5s^25p^6$ outer electronic configuration. Chemical reagents can hardly disturb these *f*-electrons. Therefore the lanthanides exhibit a dominant +3 state. Rarely valences outside +3 are known. One such exceptional case is quadrivalent cerium. Note that the constancy of the + 3 state in the lanthanides is very much striking in view of the variable valences of the *d*-block transition elements. In the *d*-block transition elements the *d*-electrons make the penultimte shell and once the outer orbital s^2 electrons are gone the *d*-orbitals have no protection against chemical reagents.

Since the *f*-orbitals are deep seated and since all *f*-electrons have the same radial distribution, addition of electrons to such orbitals cannot add to the size of the element. Moreover the screening efficiency of different orbitals follows the order $s > p > d > f$. Thus the enhanced nuclear charge (due to increase in atomic number) is heavily felt by the outer orbitals because of inefficient screening by the *f*-electrons. Addition of new *f*-orbital electrons cannot compensate the effect of increasing nuclear charge. This leads to a contraction in the size of the atoms and ions. Contraction is also observed in the *d*-block transition elements but is most distinctly seen in the lanthanides. The contraction in size of the lanthanides with increasing atomic number is known as *lanthanide contraction* (Table 22.5).

Table 22.5. Lanthanide Contraction

Element	Atomic Number	M^{3+} Electronic Configuration	First Ionisation Potential (*ev*)	M^{3+} Radius (A)
La	57	[Pd] $4f^0 5s^2 5p^6$	5.61	1.06
Ce	58	[Pd] $4f^1 5s^2 5p^6$	5.60	1.03
Pr	59	[Pd] $4f^2 5s^2 5p^6$	5.48	1.01
Nd	60	[Pd] $4f^3 5s^2 5p^6$	5.5	1.00
Pm	61	[Pd] $4f^4 5s^2 5p^6$	. . .	0.98
Sm	62	[Pd] $4f^5 5s^2 5p^6$	5.60	0.96
Eu	63	[Pd] $4f^6 5s^2 5p^6$	5.67	0.95
Gd	64	[Pd] $4f^7 5s^2 5p^6$	6.16	0.94
Tb	65	[Pd] $4f^8 5s^2 5p^6$	5.98	0.92
Dy	66	[Pd] $4f^9 5s^2 5p^6$	. . .	0.91
Ho	67	[Pd] $4f^{10} 5s^2 5p^6$	. . .	0.89
Er	68	[Pd] $4f^{11} 5s^2 5p^6$	6.08	0.88
Tm	69	[Pd] $4f^{12} 5s^2 5p^6$	5.81	0.87
Yb	70	[Pd] $4f^{13} 5s^2 5p^6$	6.22	0.86
Lu	71	[Pd] $4f^{14} 5s^2 5p^6$	6.15	0.85

In keeping with the gradually decreasing size from lanthanum to lutecium the standard electrode potentials (M^{3+}/M) of the lanthanides register an increase from lanthanum (−2.52 volts) to lutecium (−2.25 volts) (Table 22.6). The magnitude of the standard potentials, however, indicate that the lanthanides are pretty strong basic elements. Their ionisation potentials also register a gradual increase from lanthanum (5.61 *ev*) to lutecium (6.15 *ev*) though not in a graded manner. Note that whereas in all Periodic groups the basic properties increase with increasing atomic number in the lanthanides the reverse holds i.e. lanthanum (III) is the most basic while lutecium (III) is the least basic..

As expected of ionic fluorides the melting points of the trivalent lanthanide fluorides are the highest in the series of the four halides. But the melting point ordering of the other three halides is quite unexpected: $MI_3 > MBr_3 > MCl_3$.

The lanthanum hydroxides are sparingly soluble: ($La(OH)_3$, $K_{SP} 1.0 \times 10^{-19}$; $Lu(OH)_3$, $K_{SP} 2.5 \times 10^{-24}$) and are precipitated by NaOH, and by the addition of NH_4OH even in the presence of NH_4Cl. The hydroxides are converted to Ln_2O_3 on heating. Lanthanum hydroxide is the strongest base among the lanthanides and absorb CO_2 from air. Lanthanide (M^{3+}) ions do not form alum type double sulphates. This is due to their large size compared to other M^{3+} ions (Al^{3+}, 0.52A and $Ln^{3+} > 0.85A$). It is easier to have $6H_2O$ firmly coordinated to the smaller Al^{3+} than it is to the Ln^{3+} ions.

For the *d*-block transition elements the incompletely filled *d*-orbitals are exposed to the ligand lone pairs in coordination complexes. As a consequence, crystal field effects are substantial and hence magnetic properties and electronic spectra can give valuable informations on the stereochemistry of these complexes. On the contrary, in the lanthanides the incompletely filled 4*f* shell is deep seated and are hardly affected by the ligand lone pairs. Hence crystal field effects in lanthanide complexes are minimal. Magnetic properties and electronic spectra are hardly of any usefulness in the identification of stereochemistry in lanthanide complexes. The only dependable evidence can be had from a thorough X-ray crystallographic structure determination. However in neodymium (III) complexes the ${}^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition is hypersensitive to ligand and solvent environment. It has now been possible to have the shapes of this hypersensitive band of some neodymium (III) complexes of varying coordination numbers, for which the geometries are also known through X-ray diffraction. Thus shapes of this hyper sensitive transition in new neodymium (III) complexes are first evaluated, then matched with the authentic spectra of complexes of known coordination geometry and final conclusions are then drawn about the stereochemistry of the new syntheses. Short of X-ray this is the best that a coordination chemist can do.

Although the charge on the lanthanides is high (+3) the size is also large (cf: Cr^{3+}, 0.6*A*; Ln^{3+}, 0.85 to 1.06*A*). Hence their complexing ability is generally assumed to be less than the *d*-block elements. Because of the poor crystal field effect stereochemical studies through magnetic properties and electronic properties provide little information. A consequence of the comparatively large size is a wide range of coordination numbers 6, 7, 8, 9, etc. It was earlier believed that the lanthanides prefer to give complexes with oxygen donor ligands. However studies conducted in recent times has revealed that the lanthanides do form complexes with wide range of polydentate ligands having oxygen and nitrogen donor centres. Complexes with chelating ligands such as oxin, EDTA, β-diketones are well-known: Na[Ln(EDTA)]; $Ln[Ln(EDTA)]_3$; $[Ln(acac)_3)]$. Recently a wide range of multidentate schiff bases with oxygen and nitrogen donor atoms. have raised, in many cases, the coordination number beyond 6. For example, a tridentate monobasic (ONN) ligand 2-benzoylpyridine 2-benzoylhydrazone (LH) gives complexes of the type [LnL$_3$] with a coordination number 9. The lanthanides being highly electropositive cannot back donate and hence their complexes with π-acid ligands such as CO, CNR, NO, PR$_3$, etc are unknown. Complexes of the type [Ln(o-phen)$_3$](SCN)$_3$ are known however, but these surely have no π-bond between the metal and the aromatic ring.

The partly filled *f*-subshell electrons of the lanthanides are not disturbed by ligands. Hence their magnetochemistry is not dominated by crystal fields. The *f*-electrons are all free to undergo strong L and S coupling giving resultant J which then decides the value of the magnetic moment (Chapter 11):

$$\mu_J = g\sqrt{J(J+1)}\beta \text{ where } g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$

Only samarium and europium do not obey this simple equation since their excited states lie close to the ground state so that both the ground state and the excited states are populated according to Maxwell Boltzmann distribution law. These aspects have been considered in Chapter 11. A double-hump curve of magnetic moments against atomic numbers of the lanthanides is finally obtained (Chapter 11). Table 22.6 records some of the above discussed properties of the lanthanides.

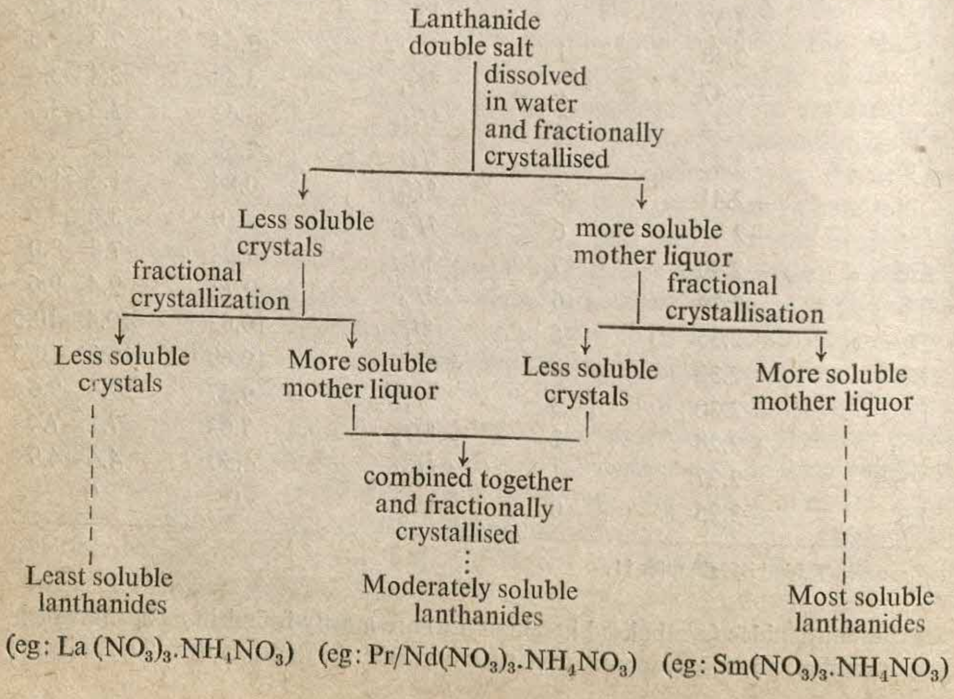
Table 22.6. Some More Properties of the Lanthanides

Element	$E°$(volts) $M^{3+}+3e \rightleftharpoons M$	Unpaired electrons in M^{3+} state	Ground state symbol of M^{3+}	Magnetic* moment of M^{3+}; $\mu_J = g\beta\sqrt{J(J+1)}$	Magnetic moment (experimental)
La	−2.52	0	$^1S_0$	0	0 B.M.
Ce	−2.48	1	$^2F_{5/2}$	2.54	2.3−2.5
Pr	−2.47	2	$^3H_4$	3.58	3.4−3.6
Nd	−2.44	3	$^4I_{9/2}$	3.62	3.5−3.6
Pm	−2.42	4	$^5I_4$	2.68	—
Sm	−2.41	5	$^6H_{5/2}$	0.84	1.5−1.6
Eu	−2.41	6	$^7F_0$	0	3.4−3.6
Gd	−2.40	7	$^8S_{7/2}$	7.94	7.8−8.0
Tb	−2.39	6	$^7F_6$	9.72	9.4−9.6
Dy	−2.35	5	$^6H_{15/2}$	10.63	10.4−10.5
Ho	−2.32	4	$^5I_8$	10.60	10.3−10.5
Er	−2.30	3	$^4I_{15/2}$	9.57	9.4−9.6
Tm	−2.28	2	$^3H_6$	7.63	7.1−7.4
Yb	−2.27	1	$^2F_{7/2}$	4.50	4.4−4.9
Lu	−2.25	0	$^1S_0$	0	0

* see also Table 11.5, Chapter 11.

The lanthanides (symbolised herein as Ln) are mostly found in *monazite* which is a complex phosphate containing thorium and the lanthanides. The mineral is chiefly worked out for thorium, and the lanthanides are obtained as by-product. Monazite is largely found in Kerala (India), Brazil and USA. The mineral is heated with concentrated H_2SO_4 whereby thorium and the lanthanides are converted to sulphates. The resulting pasty mass is separated by centrifugation and is dissolved in water. The solution is then neutralised to precipitate thorium, zirconium and titanium. On boiling the filtrate the lanthanide sulphates undergo hydrolysis and are precipitated as $Ln(OH)_3$. The hydroxides are then converted to a suitable double salt or to some suitable salt, and the individual rare earths separated as described below. Instead of precipitating the lanthanides as $Ln(OH)_3$, the filtrate after sepatation of thorium, zirconium and titanium may also be treated with Na_2SO_4. The light lanthanides (La to Sm) separate as sparingly soluble double sulphates of sodium and the lanthanides. The heavy lanthanides (Gd to Lu) remain in solution. The precipitate of the double sulphates may be fractionally crystallised. The heavy lanthanides remaining in solution may be separated by the fractional crystallisation of double lanthanide ammonium oxalate.

We have already mentioned in chapter 2 that the fifteen lanthanides have been allotted one single position in Group IIIA of the Periodic Table. The lanthanides have very close chemistry. Their separation from one another involved great difficulties. The old classical techniques were based on hundreds of fractional crystallisation of suitable salts such as ammonium lanthanide double nitrate, ammonium lanthanide double sulphate etc. The end fractions containing the most soluble and the least soluble lanthanides, and the middle fractions were separately dissolved in water and refractionated.


Lanthanide double salt
dissolved in water and fractionally crystallised
Less soluble crystals
more soluble mother liquor
fractional crystallization
fractional crystallisation
Less soluble crystals
More soluble mother liquor
Less soluble crystals
More soluble mother liquor
combined together and fractionally crystallised
Least soluble lanthanides
Moderately soluble lanthanides
Most soluble lanthanides
(eg: La $(NO_3)_3.NH_4NO_3$)
(eg: Pr/Nd$(NO_3)_3.NH_4NO_3$)
(eg: Sm$(NO_3)_3.NH_4NO_3$)

After hundreds of such fractional crystallisations reasonably pure samples could be obtained.

Nowadays lanthanides are separated by solvent extrtaction or by ion-exchange techniques.

Solvent Extraction Technique: The lanthanides can be extracted from aqueous nitric acid solution by the organic extractant tributyl phosphate (TBP):

$$Ln^{3+}(aq)+3NO_3^-(aq)+3TBP(org) \rightleftharpoons Ln(NO_3)_3(TBP)_3(org)$$

where *aq* and *org* stand for the aqueous and the organic phases. Expectedly the extraction is enhanced with decreasing ionic radius (i.e. with increasing atomic number) since decreasing radius is an index of increasing complexation. Regulating the conditions of the extraction and proper choice of the extracting reagent lead to a staisfactory separation of the lanthanides.

The efficiency of such separation depends on the distribution coefficient (D) of the individual lanthanides between the two liquid phases:

$$D = \frac{C_{Ln(NO_3)_3(TBP)_3(org)}}{C_{Ln^{3+}(aq)}}$$

If we choose two lanthanides Ln and Ln′ with distribution coefficients D and D′ respectively then we have:

$$\text{separation factor } \alpha = \frac{D'}{D}$$

$$= \frac{C_{L'n(NO_3)_3(TBP)_3(org)}}{C_{L'n^{3+}(aq)}} \times \frac{C_{Ln^{3+}(aq)}}{C_{Ln(NO_3)_3(TBP)_3(org)}}$$

The equilibrium constant K of an individual extraction is given by:

$$K = \frac{C_{Ln(NG_3)_3(TBP)_3(org)}}{C_{Ln^{3+}(aq)} . C^3{}_{NO_3^-(aq)} C^3{}_{TBP(org)}}$$

Then simple manipulation gives:

$$D = K . C^3{}_{NO_3^-(aq)} . C^3{}_{TBP(org)}$$

$$\therefore \log D = \log K + 3 \log C_{NO_3^-(aq)} + 3 \log C_{TBP(org)}$$

If concentration of TBP is maintained constant but concentration of NO_3^- (*aq*) is varied, then a plot of log D against log $C_{NO_3^-(aq)}$ will produce a straight line of slope 3 and intercept log K. Such studies indeed produce a straight line.

Heavier lanthanides with smaller ionic radius and hence with greater complexing ability prefer to be extracted into the organic phase while the lighter lanthanides (with larger ionic radius) prefer to remain in the aqueous phase.

Ion Exchange Resin Techniqne: Separation on an ion exchange resin bed involves passing a mixture of the lanthanides through a column of cation exchange resin in the H^+ form. The lanthanides are held on the resin (HR) bed:

$$3HR+Ln^{3+} \rightleftharpoons 3H^+ + LnR_3$$

Lanthanium (III) has the largest ionic size while lutecium (III) has the smallest size. The hydrated lanthanium (III) is thus the smallest and hydrated lutecium (III) is the biggest. Therefore lanthanium (III) will be strongly held while lutecium (III) will be weakly held on the resin bed. The lanthanides are then eluted with a suitable complexing agent solution. By regulating the pH and the complexing agent concentration effective separation of the different lanthanides has been achieved.

The distribution coefficient, D_0, is expressed as:

$$D_0 = \frac{C_{Ln^{3+}(R)}}{C_{Ln^{3+}(aq)}} \text{ (where R = resin phase; } aq \text{ = aqueous phase)}$$

For a second lanthanide L′n we have:

$$D'_0 = \frac{C_{L'n^{3+}(R)}}{C_{L'n^{3+}(aq)}}$$

and separation factor $\alpha = \frac{D'_0}{D_0} = \frac{C_{L'n^{3+}(R)}}{C_{L'n^{3+}(aq)}} \times \frac{C_{Ln^{3+}(aq)}}{C_{Ln^{3+}(R)}}$

On the addition of a complexing (usually chelating) agent AA new equilibria will be operating:

$$Ln^{3+}(aq) + n(AA)aq \rightleftharpoons Ln^{3+}(AA)_n(aq)$$

$$L'n^{3+}(aq) + n(AA)aq \rightleftharpoons L'n^{3+}(AA)_n(aq)$$

The total concentration of a lanthanide will be made up of the concentration of the complexed and uncomplexed lanthanide the distribution between the resin and the aqueous phase takes the form:

$$D = \frac{C_{Ln^{3+}(R)}}{C_{Ln^{3+}(aq)} + C_{Ln^{3+}(AA)n(aq)}}$$

Again the formation constant K of the complex is given by:

$$K_{Ln^{3+}(AA)n} = \frac{C_{Ln^{3+}(AA)n(aq)}}{C_{Ln^{3+}(aq)} \times C^n_{AA(aq)}}$$

$$\therefore \; C_{Ln^{3+}(AA)n(aq)} = K_{Ln'^{3+}(AA)n} \cdot C_{Ln^{3+}(aq)} \cdot C^n_{AA(aq)}$$

Then
$$D = \frac{C_{Ln^{3+}(R)}}{C_{Ln^{3+}(aq)} + K_{Ln^{3+}(AA)n'}\, C_{Ln(aq)} . C^n_{AA(aq)}}$$

$$= \frac{C_{Ln^{3+}(R)}}{C_{Ln(aq)}} \cdot \frac{1}{1 + K_{Ln^{3+}(AA)n'}\, C^n_{AA(aq)}}$$

$$= D_o \times \frac{1}{1 + K_{Ln^{3+}(AA)n} . C^n_{AA(aq)}} = \frac{D_o}{K_{Ln^{3+}(AA)n} . C^n_{AA(aq)}}$$

(since in the denominator the last term is much greater than 1).

Thus we see that the stability of the complex very much affects the distribution ratio of a particular lanthanide. So separation factor of two lanthanides is written as:

$$a' = \frac{D'}{D} = \frac{D'_o}{K'_{Ln^{3+}(AA)_n} \cdot C^n_{AA\,(aq)}} \times \frac{K_{Ln^{3+}(AA)_n} \cdot C^n_{AA\,(aq)}}{D_o}$$

$$= \frac{D'_o}{D_o} \times \frac{K_{Ln^{3+}(AA)_n}}{K'_{L'n^{3+}(AA)_n}}$$ (The ratio of the two concentrations has been assumed to be 1).

Thus if the complexing liqand gives complexes of varying stability separation of lanthanides will be possible by elution from an ion-exchange resin column. Citric acid, ethylenediaminetetra acetic acid, nitrilotriacatic acid or alpha hydroxybutyric acid ($(CH_3)_2$ CH (OH) COOH) has been successfully used for the selective elution of the lanthanides from the resin column. The smaller sized ions eg: lutecium are more readily complexed and hence more easily eluted. The elution order is in conformity with the order of the ionic radii. Thus lutecium is eluted first while lanthanum comes off the column last. Each lanthanide has a characteristic eluate volume.

The lanthanide metals may be obtained by the electrolysis of fused chlorides or by the reduction of the anhydrous halides with stronger electropositive metals such as sodium, magnesium, etc.

22.5.2. The Actinides. The elements from actinium to lawrencium form the second series of inner transition elements. Of these the transuranic elements are all man-made elements (Chapter 12) and the studies of their chemistries were made on microgram and submicrogram levels. Prior to the syntheses and studies of the transuranic elements, actinium, thorium, protactinium and uranium were included in the Periodic Groups IIIA, IVA, VA and VIA respectively. These inclusions were warranted by their dominant valences. For example thorium behaves chemically very much like a quadrivalent transition element such as Hf. Other valences were of little consequence with thorium. Similarly uranium has a dominant valence +6. Other valences +4, +3, etc. were of lesser importance. The existence of tervalent actinium compounds and their isomorphism with those of lanthanum justified its inclusion in group IIIA. As and when the transuranic elements were known the need for a different classification arose. The overall similarities of actinium and transactinium elements to the lanthanides became evident. In keeping with the naming of the lanthanides, these elements from Ac to Lw are now called the *actinides* and are now allotted one group position in group IIIA after radium of group IIA.

Although the actinides have many overall similarities with the lanthanides they have many subtle differences as well. The actinides have a deep seated, incomplete 5*f* subshell compared to the 4*f* subshell of the lanthanides. The probable electronic configuration of the elements is shown in Table 22.6. There is an important difference between the 4*f* and the 5*f* orbitals. The radial distribution function of the 5*f* orbital shows a small shell of electron density below the main 5*f* shell (compare for example 1*s* and 2*s* radial functions; Chapter 1). Therefore the 5*f* orbitals are more penetrating than the 4*f* orbitals (Fig. 22.4). In the lanthanides the 4*f* subshell is well within the 6*s* valence subshell and also within the 5*s* subshell.

Therefore there is no question of an overlap between the $4f$-orbitals and the surrounding ligands. The $5f$-orbitals being penetrating in nature are little more diffuse at the periphery of the atom (Fig. 22.4 (*b*). Hence these orbitals are somewhat disturbed by ligands. It is well-known that the energy gaps between different levels and sublevels decrease with increasing atomic number (Chapter 1). Thus in the actinides the energies of $5f$, $6d$, $7s$, $7p$ orbitals are but equal. A natural consequence is that the bonding in actinide compounds may involve any or all of these orbitals.

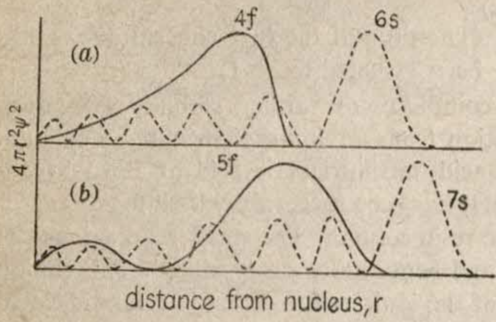


Fig. 22.4. The radial distribution function for (*a*) the $4f$, and $6s$ electrons of the lanthanides (*b*) the $5f$ and $7s$ electrons of the actinides

Like the lanthanides the actinides also show an *actinide contraction*. The ionic size is dependent mostly on two factors namely (1) the quantum number of the outermost orbital electrons and (2) the effective nuclear charge felt by these electrons. The screening effect of the $5f$ electrons cannot compensate for the additional nuclear charge with increasing atomic number. Therefore, there results a contraction in size (Table 22.7).

Table 22.7. The Actinides and Their Properties

Element	Atomic Number	Probable Electronic Configuration	M^{3+}Radius (A)	Formal Potential; $M^{3+}+3e \rightarrow M$ in 1M $HClO_4$ (volts)
Ac	89	[Rn] $6d^17s^2$	1.18	-2.60
Th	90	[Rn] $6d^27s^2$	1.14	
Pa	91	[Rn] $5f^26d^17s^2$or[Rn]$5f^16d^27s^2$	1.12	
U	92	[Rn] $5f^36d^17s^2$	1.11	-1.80
Np	93	[Rn] $5f^57s^2$	1.09	-1.83
Pu	94	[Rn] $5f^67s^2$	1.07	-2.03
Am	95	[Rn] $5f^77s^2$	1.06	-2.32
Cm	96	[Rn] $5f^76d^17s^2$		
Bk	97	[Rn] $5f^86d^17s^2$ or [Rn] $5f^97s^2$		
Cf	98	[Rn] $5f^{10}7s^2$		
Es	99	[Rn] $5f^{11}7s^2$		
Fm	100	[Rn] $5f^{12}7s^2$		
Md	101	[Rn] $5f^{13}7s^2$		
No	102	[Rn] $5f^{14}7s^2$		
Lw	103	[Rn] $5f^{14}6d^17s^2$		

Table 22.8 gives the different oxidation states of the actinides, the double underlined ones being the most stable. The commonest valences of the five elements after actinium are from +4 to +6 but following americium +3 state is the dominant one. The wider variation in the span of the valences in the actinide compounds compared to the lanthanides is a reflection of the participation of the 5*f*-orbitals also in the bonding.

The standard electrode potentials (M^{3+}/M) of the lanthanides expectedly become less negative (due to lanthanide contraction). In the actinides the M^{3+}/M potentials become less negative from actinium to uranium and then become more negative again. The redox potentials of the M^{4+}/M^{3+} couples increase with atomic number. Americium (IV) is thus more powerful an oxidant than cerium (IV) while quadrivalent plutonium, neptunium and uranium are less effective. Uranium (III) is a strong reducing agent. With the exception of uranium all valence states above + 3 are strongly oxidising.

Table 22.8. Oxidation States of the Actinides

Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Em	Md	No
$\underline{\underline{3}}$	3	3	3	3	$\underline{3}$	$\underline{\underline{3}}$	$\underline{\underline{3}}$	$\underline{\underline{3}}$	$\underline{\underline{3}}$	$\underline{\underline{3}}$	$\underline{\underline{3}}$	$\underline{\underline{3}}$	$\underline{\underline{3}}$
	$\underline{\underline{4}}$	4	4	$\underline{4}$	$\underline{\underline{4}}$	$\underline{4}$	4	$\underline{4}$					
		$\underline{\underline{5}}$	5	$\underline{\underline{5}}$	$\underline{5}$	$\underline{5}$							
			$\underline{\underline{6}}$	$\underline{6}$	$\underline{6}$	$\underline{6}$							

Unlike the lanthanides many of the actinides form oxocations such as UO_2^{2+}, UO_2^+, NpO_2^+, PuO_2^+, PaO_2^+, etc.

It has been mentioned earlier that unlike the lanthanides bonding in the actinide compounds can involve any or all of the 5*f*, 6*d*, 7*s* and 7*p* orbitals. In lanthanides we have mostly ionic bonds whereas in the actinides covalent bonding may be important. Thus the actinides can form complexes with π-bonding ligands such as thioethers, alkylphosphines as well as with usual ligands such as halides, sulphates, etc.

The magnetic properties of the actinides are more complicated than those of the lanthanides since in these heavy elements simple Russell Saunders type L-S coupling may not be strictly valid and individual j-j coupling may become important. However on applying the μ_J equation (Chapter 11) based on L-S coupling it is observed that for the same f^n configurations the actinides have somewhat lower magnetic moment values than the lanthanides. One way of explaining these lower moment values beyond the theoretically predicted values is to accept that $5f^n$ electrons of the actinides are more exposed to crystal fields which may lead to considerable quenching of the orbital contribution to the moment. The ions Pu^{3+} and Am^{3+} resemble Sm^{3+} and Eu^{3+} respectively, and their magnetic moments are those expected on the basis of thermally controlled population of both the ground state and the next available excited state.

The similarity between the lanthanides and the actinides is also exhibited by the isomorphous character of their compounds. Thus MF_3 and MCl_3 compounds of La, Nd, Ac, U, Pu, Am are isomorphous. M_2O_3 compounds of La, Nd, Ac, Pu, Am are also isomorphous. Complex KMF_5 halides of Th, U and Pu are also isomorphous.

The nitrates, perchlorates and the sulphates of the trivalent actinides and lanthanides are soluble in water whereas the hydroxides, fluorides and the carbonates are insoluble. Elution behaviours of the complex citrates or EDTA complexes of the lanthanides and the actinides on cation exchange columns are similar.

Of the actinides only thorium and uranium occur in nature in significant amounts. Actinium was originally obtained from uranium minerals in which it occurs only in very minute quantity. It is now obtained in milligram quantity by the following reactions:

$$^{226}_{88}\mathrm{Ra} + {}^{1}_{0}n \rightarrow {}^{227}_{88}\mathrm{Ra} + \gamma\,;\quad {}^{227}_{88}\mathrm{Ra} \xrightarrow[\text{half life}]{41.2\text{ min.}} {}^{227}_{89}\mathrm{Ac} + {}^{0}_{-1}e$$

Plutonium is obtained by the following nuclear reactions:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}n \rightarrow {}^{239}_{92}\mathrm{U} + \gamma\,;\quad {}^{239}_{92}\mathrm{U} \rightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}e$$

$$^{239}_{93}\mathrm{Np} \rightarrow {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}e$$

Plutonium-239 is an alpha emitter with a half life of 2.4×10^4 years. On mass scale plutonium-239 is separated from uranium and other fission products by extraction with tributylphosphate (TBP) in kerosine from an aqueous nitric acid solution. The uranyl and plutonyl nitrates go into TBP—kerosene as $MO_2(NO_3)_2 \cdot 2TBP$. The $UO_2^{2+}-PuO_2^{2+}$ mixture is then treated with aqueous SO_2 or N_2H_4 whereby PuO_2^{2+} becomes Pu^{3+} and passes into the aqueous phase. The uranium (VI) is either not reduced or only partially reduced to uranium (IV) and remains in the organic phase. The nuclear reactions leading to the syntheses of the other actinides are indicated below:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}n \rightarrow {}^{237}_{92}\mathrm{U} + 2\,{}^{1}_{0}n\,;\quad {}^{237}_{92}\mathrm{U} \rightarrow {}^{237}_{93}\mathrm{Np} + {}^{0}_{-1}e$$

$$^{239}_{94}\mathrm{Pu} + {}^{1}_{0}n \rightarrow {}^{240}_{94}\mathrm{Pu} + \gamma$$

$$^{240}_{94}\mathrm{Pu} + {}^{1}_{0}n \rightarrow {}^{241}_{94}\mathrm{Pu} + \gamma\,;\quad {}^{241}_{94}\mathrm{Pu} \rightarrow {}^{241}_{95}\mathrm{Am} + {}^{0}_{-1}e$$

$$^{241}_{95}\mathrm{Am} + {}^{1}_{0}n \rightarrow {}^{242}_{95}\mathrm{Am} + \gamma\,;\quad {}^{242}_{95}\mathrm{Am} \rightarrow {}^{242}_{96}\mathrm{Cm} + {}^{0}_{-1}e$$

$$^{241}_{95}\mathrm{Am} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{243}_{97}\mathrm{Bk} + 2\,{}^{1}_{0}n$$

$$^{242}_{96}\mathrm{Cm} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{245}_{98}\mathrm{Cf} + {}^{1}_{0}n\,.$$

Neptunium-237 is an alpha emitter with a half life of 2.25×10^6 years.

The trivalent actinides are absorbed on a suitable cation exchange resin and the absorbed cations are eluted with a suitable complexing agent such as citrate or α-hydroxy butyrate. The elution behaviour of the actinides compares well with that of the lanthanides. Concentration peaks are obtained such that the smaller and hence the more easily complexing ions at the lutecium end (for the lanthanides) and the mendeleevium end (for the actinides) emerge from the exchange column first. Individual lanthanides and actinides, therefore, emerge under controlled conditions at characteristic eluate volumes.

STUDY QUESTIONS

1. What are transition elements? How do you classify them? Discuss their special features.

2. Present a comparative survey of the transition and non-transition elements.

3. Sodium is a non-transition element whereas iron is a transition element. Make a comparative assessment of their likely physical and chemical behaviour.

4. Nickel with an atomic number 28 is a *d*-block transition element. Indicate its electronic configuration and predict its physical and chemical behaviour.

5. Explain the basis of the colour and paramagnetism of transition metal compounds.

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23

Low Oxidation States: Complexes of π-Acid Ligands

23.1. INTRODUCTION

An important feature of the transition metal chemistry is the formation of complexes. Formation of complexes with the metal ions in their common or higher oxidation states is not difficult to understand. An electrostatic attraction between the positively charged metal ion and the negative or dipolar ligands can lead to the formation of a complex. Ligand lone pairs take suitable stereochemical positions and perturb the metal *d*-orbitals. A separation in energy of the *d*-orbitals occurs (crystal field theory, Chapter 10). The ligand lone pairs may, alternatively, be assumed to overlap suitable empty hybridised orbitals of the metal ion (valence bond theory, Chapters 10 and 11). Such metal-ligand bonds are formed along the metal-ligand bond axes with the electron density concentrated symmetrically along the bond axis. These are sigma (σ) metal-ligand bonds. Such overlap of orbitals will make the bonds substantially covalent, particularly if the complex is an inner orbital complex (Chapters 10 and 11).

We run into difficulties with the above sort of mechanisms while explaining the formation of complexes in low-valent states. While the metal is in zero or negative oxidation state there can be no attractive mechanism between the metal and the ligands, as is possible for a positively charged metal ion. The bonding in low oxidation states is largely covalent through some sort of overlap of ligand orbitals and metal orbitals. The formation of a sigma bond by the overlap of a lone pair orbital of the ligand with an empty orbital of the metal leads to excessive negative charge accumulation on the metal if the metal is already in a zero or negative oxidation state. This is a situation which is not welcome by the metal since it leads to substantial repulsion between negative charges of the metal and of the ligands. However, the charge accumulation on the metal can be countered by transfering some charge from the metal to the ligand, again by a suitable overlap of a filled metal orbital and empty π-type ligand orbital. *Ligands which possess suitable empty orbitals to receive back donated electrons from the metals are the most suitable ones for stabilisation of low oxidation states of metals.* In effect therefore we have a double bonding—a sigma bond between a filled ligand orbital and an empty metal orbital, and a π-bond between a filled metal orbital and an empty ligand (π-type) orbital.

Ligands which have been found to stabilise low oxidation states of metals include CO, NO, CN^-, isocyanides $C = N-R$, R_3P, R_3As, $\alpha\alpha'$-dipyridyl, o-phenanthroline and unsaturated organic molecules. All these ligands have filled donor orbitals as also empty acceptor orbitals. Note that among the above ligands we do not have any tricovalent, tetrahedral nitrogen compounds such as NH_3 or ethylenediamine (en). This is because nitrogen, being a member of the second period, does not have any *d*-orbital where back donated electrons from a low-valent metal can be accommodated. Its valence shell in NH_3 or en is an octet consisting of three shared pairs and a fourth unshared lone pair of electrons. So NH_3 or en can function only as a sigma donor but not as a π-acceptor. Hençe ammonia or ethylenediamine is useless in low oxidation stabilisation.

Carbon monoxide is normally a poor donor as revealed by its poor basic strength. For instance CO does not form an adduct even with a very strong Lewis acid (electron acceptor) BF_3. But it forms a long series of metal carbonyls. This improved behaviour in presence of low-valent metals is due to the fact that on back donation from the metal to the ligand, the otherwise poor donor CO now becomes a substantially better donor. This effect is called a *synergic effect*.

Complexes with CO, NO, CNR, PR_3, etc. are also called π-acid complexes since the metal to ligand bond is of the π-type and the ligand behaves as a π-acid as it can receive back donated electrons from the low oxidation state metal into its π-orbitals. *Note that in such complexes both the metal and the ligand function both as donors and acceptors.*

23.2 METAL CARBONYLS

Carbon monoxide forms complexes with several transition metals in low oxidation states. These complexes are called carbonyls which are of two types: mononuclear and polynuclear carbonyls. Some metal carbonyls are known to give important derivatives. On treatment with halogens carbonyl halides are formed. Carbonyl hydrides are formed on alkaline hydrolysis of carbonyls. Metal carbonyls are also known to give mixed ligand complexes with other π-acid ligands such as NO, PR_3, $C = N-R$, etc.

23.2.1. Syntheses of Metal Carbonyls. The following methods are useful:

(1) *Interaction of carbon monoxide with the finely divided freshly reduced transition metals under suitable pressure and temperature:* nickel carbonyl is very readily formed from nickel and carbon monoxide at ordinary temperature and pressure. It may be interesting to note that Mond, a British Engineer, while working with carbon monoxide first noted that valves made of nickel were being

readily affected. His studies led to the discovery of nickel tetracarbonyl, the very first carbonyl to be made and studied.

$$Ni + 4CO \xrightarrow{\text{ordinary pressure and temperature}} Ni(CO)_4$$

$$Fe + 5CO \xrightarrow{200^\circ C/100 \text{ atm. pressure}} Fe(CO)_5$$

Iron carbonyl can be made in low yield at ordinary temperature and pressure in presence of carriers such as Plaster of Paris, barium sulphate etc. Iron pentacarbonyl is absorbed by finely divided reduced iron and the access of further carbon monoxide to the metal surface is blocked and the reaction is inhibited. The use of a carrier for reduced metal is likely to tide over this difficulty. The carrier may also act as a catalyst.

(2) *Interaction of a suitable metal salt and carbon monoxide in the presence of a reducing agent:*

$$2CoCO_3 + 8CO \xrightarrow[\sim 150^\circ C/250 \text{ atm. pressure}]{2H_2} Co_2(CO)_8 + 2CO_2 + 2H_2O$$

$$MoCl_5 + 6CO \xrightarrow{5Na \text{ in diglyme}} Mo(CO)_6 + 5NaCl$$

$$CrCl_3 + 6CO \xrightarrow{Et_3Al \text{ in ether}} Cr(CO)_6$$

$$Re_2S_7 + 10CO \xrightarrow{250^\circ C/200 \text{ atm. pressure}} Re_2(CO)_{10} + 7S$$

(3) *Syntheses of polynuclear carbonyls from mononuclear carbonyls:*

$$2Fe(CO)_5 \xrightarrow{\text{ultraviolet light}} Fe_2(CO)_9 + CO$$

(4) *Interaction of a metal carbonyl with another metal halide:*

$$WCl_6 + 3Fe(CO)_5 \xrightarrow[\text{ether}]{90^\circ C} W(CO)_6 + 3FeCl_2 + 9CO$$

Table 23.1. gives some binary carbonyls of the first transition series.

Table 23.1. Metal Carbonyls of the First Transition Series

V	VI	VII	VIII		
$V(CO)_6$ Black crystals: decomposes at 70°C; can be sublimed in vacuo. It is paramagnetic (one spin).	$Cr(CO)_6$ Colourless crystals; can be sublimed in vacuo; decomposes at 180-200°C. It is diamagnetic.	$Mn_2(CO)_{10}$ Golden crystals; melts at 154-155°C; can be sublimed in vacuo. It is diamagnetic.	$Fe(CO)_5$ Yellow liquid; B.P. 103°C. It is diamagnetic.	$Co_2(CO)_8$ Orange crystals; B.P. 103°C. It is diamagnetic.	$Ni(CO)_4$ Colourless liquid; B.P.43°C. It is diamagnetic.
			$Fe_2(CO)_9$ Bronze plates; decomposes at 100°C.	$Co_4(CO)_{12}$ Black crystals; decomposes at 60°C.	

23.2.2. Reactions of Metal Carbonyls. The reactions of metal carbonyls are enormously varied. We enumerate only a few of the more important ones. Alkaline hydrolysis of iron pentacarbonyl leads to yellow carbonyl hydride anion in which iron has −2 oxidation state:

$$Fe(CO)_5 + 3NaOH \rightarrow Na[HFe(CO)_4] + Na_2CO_3 + H_2O$$

Reduction of metal carbonyls by suitable reductants gives carbonylate anions:

$$Co_2(CO)_8 + 2Na \xrightarrow{\text{tetrahydrofuran}} 2Na[Co(CO)_4]$$

$$Mn_2(CO)_{10} + 2Li \xrightarrow{\text{tetrahydrofuran}} 2Li[Mn(CO)_5]$$

Carbonyl halides are obtained by the direct reaction of carbon monoxide and metal halides, or by the reaction of halogens on metal carbonyls:

$$RuI_3 + 2CO \xrightarrow{200°C} [Ru(CO)_2I_2]_n + \tfrac{1}{2}I_2$$

$$Fe(CO)_5 + I_2 \longrightarrow [Fe(CO)_4I_2] + CO$$

Reactions with other π-acid ligands under suitable conditions gives mixed complexes:

$$Fe(CO)_5 + 2PR_3 \rightarrow [Fe(CO)_3(PR_3)_2] + 2CO$$

$$Fe_2(CO)_9 + 4NO \rightarrow 2[Fe(CO)_2(NO)_2] + 5CO$$

23.2.3. Bonding in Metal Carbonyls. The simple metal carbonyls conform to noble gas electron number. Taking carbon monoxide as a two electron donor the electron shell of the metal in carbonyls attains the electron number of the next noble gas (Table 23.2). Thus coordination number of the metal in a metal carbonyl is dictated by the inherent desire of the metal to attain the next noble gas electron number. Nickel therefore will not form a hexacarbonyl. Cobalt and manganese having odd atomic numbers 27 and 25 therefore form dinuclear carbonyls $Co_2(CO)_8$ and $Mn_2(CO)_{10}$. The noble gas electron number is attained on assuming a metal—metal bond:

$$(CO)_4Co-Co(CO)_4 \text{ and } (CO)_5Mn-Mn(CO)_5$$

Table 23.2. Electron Shell in Metal Carbonyls

Carbonyls	Metal Electrons	Electrons donated by CO groups	Total electrons	Noble gas electron number
$Ni(CO)_4$	28	4×2	36	36(Kr)
$Fe(CO)_5$	26	5×2	36	36(Kr)
$Cr(CO)_6$	24	6×2	36	36(Kr)
$Mo(CO)_6$	42	6×2	54	54(Xe)

The 18-electron rule: This is an alternative way of expressing noble gas electron number rule (also known as the *effective atomic number rule*). The 18-electron rule means attainment of 18 electrons in the valence shell of the metal atom by saturation of the $(n-1)d$, ns and np subshells. Saturation will give $10+2+6 = 18$ electrons. Thus in $Ni(CO)_4$, Ni(O) has 10 electrons in the $3d$ valence shell and gets $4\times 2 = 8$ electrons from the four CO groups thus reaching 18 electron valence shell electronic configuration. Similarly Fe(O) has 8 electrons in the $3d$ valence shell and acquires another 10 electrons from the five CO groups thus completing the 18 electron valence shell electron configuration.

Carbon monoxide has a total of ten electrons in the outer orbitals. On hybridisation model we assume both carbon and oxygen to have sp hybridisation:

$$\mathrm{C}\quad \underset{2s}{\underline{\uparrow\downarrow}}\ \underset{2p_x}{\underline{\uparrow}}\ \underset{2p_y}{\underline{\uparrow}}\ \underset{2p_z}{\underline{\quad}}\quad \text{hybridises to}\quad \underset{2(sp_x)}{\underline{\uparrow\downarrow}}\ \ \underset{2(sp_x)}{\underline{\uparrow}}\ \ \underset{2p_y}{\underline{\uparrow}}\ \ \underset{2p_z}{\underline{\quad}}$$

$$\mathrm{O}\quad \underset{2s}{\underline{\uparrow\downarrow}}\ \underset{2p_x}{\underline{\uparrow\downarrow}}\ \underset{2p_y}{\underline{\uparrow}}\ \underset{2p_z}{\underline{\uparrow}}\quad \text{hybridises to}\quad \underset{2(sp_x)}{\underline{\uparrow\downarrow}}\ \ \underset{2(sp_x)}{\underline{\uparrow}}\ \ \underset{2p_y}{\underline{\uparrow}}\ \ \underset{2p_z}{\underline{\uparrow\downarrow}}$$

The paired electrons in sp orbitals of carbon and oxygen make the lone pairs. The other sp orbitals of carbon and oxygen overlap along the bond axis to form the sigma bond. The two p_y orbitals with one electron on each overlap to form the shared pair π-bond. The electron pair on the p_z orbital of oxygen overlap with the empty p_z orbital of carbon forming the second π-bond. This last one is of the coordinate type. Carbon monoxide (bond length 1.13A) therefore has the following structure on the hybridised model:

$$:\mathrm{C}\overset{\longleftarrow}{\underline{\underline{\qquad}}}\mathrm{O}:$$

Molecular orbital approach provides a more graphic picture of carbon monoxide. On the M.O. model the two sp_x hybrid orbitals of oxygen and carbon will combine to give two molecular orbitals: one is of the sigma bonding type (low energy) being occupied by two electrons, and the other of the high energy sigma antibonding type. The two p_y orbitals will combine to give two π-type molecular orbitals: one is of the bonding type (low energy) being occupied by two electrons, and the other of the antibonding type. Similarly the two p_z orbitals of carbon and

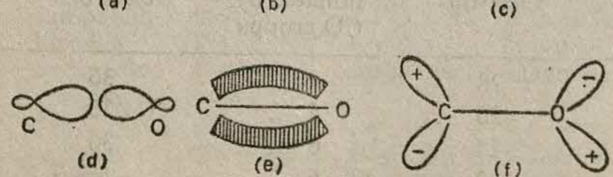

FIG. 23.1. Molecular orbitals of carbon monoxide

(*a*) carbon σsp_x lone pair (*b*) oxygen σsp_x lone pair (*c*) σsp_x bonding M.O. (*d*) σsp_x anti-bonding empty M.O. (*e*) πp_y bonding M.O. There is another similar πp_z bonding M.O. (*f*) πp_y antibonding empty M.O. There is another similar πp_z antibonding empty M.O.

oxygen will give two molecular orbitals. The bonding type M.O. is occupied by two electrons and the antibonding type is empty. The two πp_y* and πp_z* orbitals are of equal energy since p_y and p_z atomic orbitals are degenerate. The overall position in CO is that all the bonding M.O.'s are filled (Fig. 5.9; Table 5.3, Chapter 5). There are three antibonding orbitals of which the sp_x* one is of much higher energy. This particular M.O. is along the C−O bond axis and is not accessible to back donated metal electrons due to its being screened by the other π-bonding M.O.'s. The other two π-antibonding M.O.'s are available to the metal electrons. The different M.O.'s are shown in Fig. 23.1.

Since oxygen is more electronegative than carbon it is more likely that carbon lone pair will function as the donor. Structural studies show that the metal is linked to carbon. Below we represent the bonding in metal carbonyls with special reference to nickel tetracarbonyl. $Ni(CO)_4$ is tetrahedral with C−Ni−C bond angles being ~109°. This means that nickel(0) has sp^3 hybrid orbitals for sigma overlap with the four lone pairs of the four CO molecules. The metal *d*-orbitals are available for back bonding but their number will depend on the stereochemistry of the complex. In an octahedral complex (say $Cr(CO)_6$) the d_{xy}, d_{xz}, d_{yz}, are suitable for π-bonding since the other two *d*-orbitals of chromium, namely $d_{x^2-y^2}$ and d_{z^2}, are needed to form the octahedral hybrid orbitals d^2sp^3. In a tetrahedral complex, such as in $Ni(CO)_4$, none of the nickel *d*-orbitals is used in the hybridisation but the orientation of the *d*-orbitals relative to the four tetrahedral nickel-CO bonds makes the $d_{x^2-y^2}$ and d_{z^2} orbitals *more suitable* for π-overlap with the π* antibonding orbitals of CO. It follows then that there are favoured two Ni→CO bonds. Through resonance an average bond order of 1.5 between nickel and CO is established since there are four Ni←CO sigma bonds and two Ni→CO π-bonds to be averaged over four nickel-carbon links. Similar arguments will predict an average bond order of 1.5 for $Cr(CO)_6$.

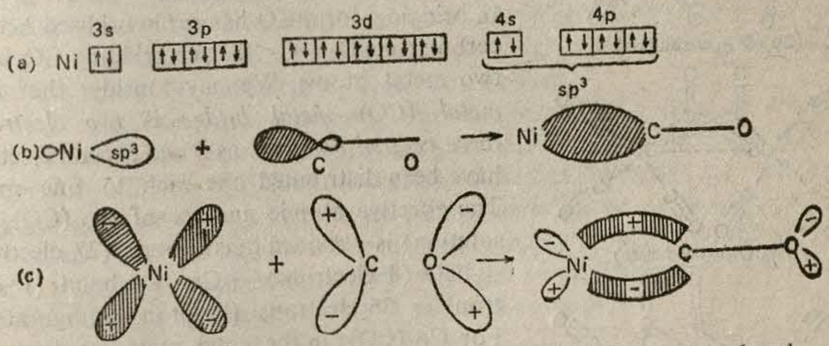

FIG. 23.2. Pictorial representation of metal-ligand bonding in nickel tetracarbonyl
(*a*) hybridisation of 4*s* and 4*p* orbitals of nickel (0)
(*b*) sigma donation from carbon to nickel (0)
(*c*) pi donation from filled nickel (0) *d*-orbitals to empty CO π* molecular orbital

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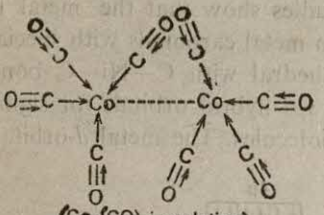
* The p_y gnd p_z atomic orbitals of any one element (C or O) are truly degenerate but then the p_y and p_z atomic orbitals of O are expected to have slightly lower energy than the p_y and p_z atomic orbitals of C because of higher nuclear charge.

Multiple bonding between nickel and CO was also proposed by Pauling on the valence bond model. The following three resonating structures were suggested. Only those electrons of nickel that participate in bonding with CO are shown (marked x). The ligand electrons are marked as dots.

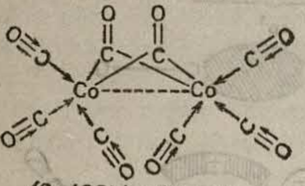
$$\text{Ni}^-\ {:}\text{C}\ \vdots\vdots\ \text{O}^+{:} \qquad \text{Ni}^-{:}\text{C}^+{::}\ddot{\text{O}}{:} \qquad \text{Ni}\overset{\times}{\underset{\times}{}}{:}\text{C}{::}\ddot{\text{O}}{:}$$

$$(\text{Ni}^- \leftarrow \text{C} \underset{=}{\leftarrow} \text{O}^+) \qquad (\text{Ni}^- \leftarrow \text{C}^+ = \text{O} \qquad (\text{Ni} = \text{C} = \text{O})$$

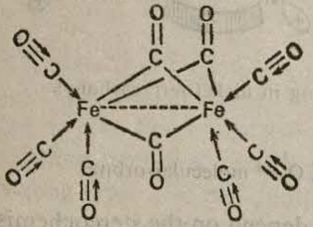
23.2.4. Some Binuclear Carbonyls: In some binuclear carbonyls like $Co_2(CO)_8$ (in solution) and $Mn_2(CO)_{10}$ all the CO molecules are terminal and get attached to the metal atom through the lone pair on the carbon. There is, however, a metal—metal bond in order to achieve the effective atomic number of the next noble gas. In binuclear carbonyls like $Fe_2(CO)_9$ and $Co_2(CO)_8$ (in the solid state) there are both terminal and bridging CO groups. In bridging form CO has sp^2 hybridised ketonic carbon (like O = C<). Each bridging CO holds two metal atoms. We may consider that each *metal*—(CO)—*metal bridge* is *two electron—three centred bond i.e.* as if two carbon electrons have been distributed one each to one metal. The effective atomic number of $Co_2(CO)_8$ (in solution) is obtained thus: cobalt (27 electrons) +4CO (8 electrons) +Co—Co bond (1 electron) = 36 electrons (krypton configuration). For $Co_2(CO)_8$ in the solid state we have per cobalt atom: cobalt (27 electrons) +3 terminal CO lone pairs (6 electrons) +2 bridging CO (2 electrons) +Co—Co bond (1 electron) = 36 electrons (krypton configuration).



($Co_2(CO)_8$ in solution)



($Co_2(CO)_8$ in solid state)



$Fe_2(CO)_9$

FIG. 23.3. Structures of $Co_2(CO)_8$ (in solution and solid state) and $Fe_2(CO)_9$.

23.2.5. Evidence of Multiple Bonding. There are several lines of evidence of the multiple bonding in metal carbonyls. We discuss below some of these:

1. Ni° and Zn^{3+} are isoelectronic; Ni^0 forms a tetracarbonyl but Zn^{2+} forms no carbonyl complex. If carbon to metal sigma bond alone were important, zinc by virtue of its double charge would have formed such a bond more easily. On the contrary if metal to carbon pi bond is also involved it is the nickel (0) that would form the bond better. Zinc (II) would surely not back-donate. Absence of $[Zn(CO)_4]^{2+}$ thus points to the importance of multiple bonding in carbonyls.

2. Increasing multiplicity of bonds decreases the bond length. If a double bond exists between the zerovalent metal and *sp* hybridised carbon then the metal-carbon bond length must be far shorter than the sum of the single bond radii of *sp* carbon and the zerovalent metal. Cotton has proved the point decisively. Prior

to Cotton's work (1965) there was no record of the radius of a zerovalent metal in the literature. Cotton synthesised a mixed diethylenetriamine ($NH_2-CH_2-CH_2-NH-CH_2-CH_2-NH_2$, dien) carbonyl complex of molybdenum (0) namely [Mo(dien) $(CO)_3$] by the action of dien on $Mo(CO)_6$. Of the six bonds of octahedral molybdenum (0) three are to the three tetrahedral nitrogen which cannot participate in double bonding. The other three bonds alone can admit of double bonding. The crystal structure and the bond distances were accurately determined. Mo$-$N distance was found to be 2.32A from which on subtraction of the covalent radius of sp^3 nitrogen ($\sim$0.7A) we get the radius of the zerovalent molybdemum to be $\sim$1.62A. Covalent radius of *sp* hybridised carbon is also $\sim$0.7A. This means if Mo$-$C bond were only single bond the bond length would have been $\sim$2.32A Measured Mo$-$C bond length in the above mixed complex is only $\sim$1.94A, far shorter than a single bond.

3. CO molecule has a characteristic carbonyl stretching frequency at 2143 cm^{-1} Due to back bonding electron density from low-valent metals is fed into the π^* antibonding orbitals. Hence CO bond order (Chapter 5) is lowered which is evident from a lowering of the stretching frequency: $Cr(CO)_6$, 2100 cm^{-1}; $V(CO)_6^-$, 1860 cm^{-1}; $Ni(CO)_4$, 2060 cm^{-1}; $Co(CO)_4^-$, 1890 cm^{-1}.

In a mixed complex containing CO and some non-π bonding ligands, like diethylenetriamine (eg: Mo(dien) $(CO)_3$), the carbonyl stretch is very appreciably lowered ($\sim$1760 cm^{-1}). This is due to the fact that the metal and the fewer CO groups can now engage in stronger π-bonding effect so as to effectively relieve the metal from the accumulating negative charge density. Lowering of bond order leads to a lengthening of carbon-oxygen bond. Thus the C$-$O bond length increases from 1.13A in CO to 1.15A in metal carbonyls.

23.3. METAL NITROSYLS

These are complexes of metal ions in low oxidation state with nitric oxide. NO is an odd electron molecule and loses the odd electron rather easily giving nitrosyl cation as evidenced by compounds $[NO]HSO_4$, $[NO]BF_4$, $[NO]ClO_4$ (Chapter 18). In nitrosyl complexes NO can participate in two ways: (1) *linear nitrosyls:* In this most prevalent cases the neutral NO molecule first transfers its odd electron completely to the metal thus reducing the metal valence by one unit. Thereafter the nitrosyl cation (also called nitrosonium ion) NO^+ becomes isoelectronic with CO and the nature of bonding between the (reduced) metal and NO^+ becomes parallel to the bonding in metal carbonyls. In these complexes the M$-$N$-$O angle is close to 180° and the complexes are examples of linear metal nitrosyls. (2) *bent nitrosyls:* In this second less prevalent case the M$-$N$-$O angle is in the range 120$-$140° and these are considered to be complexes of NO^- with sp^2 hybridised nitrogen.

Metal nitrosyls occur mostly as mixed ligand complexes in conjunction with other π-bonding low oxidation state stabilising ligands. Pure nitrosyl complexes are much too unstable because of accumulation of too much negative charge on the metal,

23.3.1. Syntheses and Reactions of Linear Nitrosyls. Nitric oxide reacts readily with polynuclear carbonyls of iron and cobalt giving volatile red liquids, $[Co(CO)_3NO]$ and $[Fe(CO)_2(NO)_2]$:

$$Co_2(CO)_8 + 2NO \rightarrow 2[Co(CO)_3NO] + 2CO$$
$$Fe_2(CO)_9 + 4NO \rightarrow 2[Fe(CO)_2(NO)_2] + 5CO$$

Substitution reactions by other π-bonding ligands such as PR_3, $C = N-R$, o-phenanthroline on the mixed carbonyl-nitrosyls only leads to substitution of the carbonyl groups: $[Fe(NO)_2(PR_3)_2]$, $[Fe(NO)_2(CNR)_2]$, $[Fe(NO)_2(\text{o-phen})]$ etc.

Metal nitrosyl halides are obtained by the action of NO on metal halides in the presence of a suitable metal acting as halogen acceptor. They may also be obtained by the action of halogens on the nitrosyl carbonyls:

$$CoI_2 + Co + 4NO \rightarrow [Co(NO)_2I]_2$$
$$4NiI_2 + 2Zn + 4NO \rightarrow [Ni(NO)I]_4 + 2ZnI_2$$
$$2[Fe(CO)_2(NO)_2] + I_2 \rightarrow [Fe(NO)_2I]_2 + 4CO$$

These nitrosyl halides are halogen bridged and have metal-metal interaction. These can be made to react with other ligands to give monomer complexes:

$$[Fe(NO)_2X]_2 + 2L \rightarrow 2[Fe(NO)_2XL]$$
$$(L = \text{substituted phosphine, } X = \text{halogen})$$

The iron nitrosyl halides react with alkali sulphide and alkyl halides to give the dark red compounds known as Roussin's salts:

$$[Fe(NO)_2I]_2 \xrightarrow{K_2S} K_2[Fe(NO)_2S]_2 \xrightarrow{CH_3Cl} [Fe(NO)_2(SCH)_3)]_2$$

These are sulphur bridged dimers.

23.3.2. Bonding in Linear Metal Nitrosyls. Composition of the metal nitrosyls is also dictated by the attainment of the electron shell of the next noble gas (Table 23.3). In the compilation of Table 23.3 nitric oxide has been considered as a three electron donor.

Table 23.3. Electron Shell in Metal Nitrosyls

Metal Nitrosyl	Metal Electrons	Electrons donated by CO or other groups	Electrons donated by NO groups	Total Electrons	Noble gas electron number
$Co(CO)_3(NO)$	27	6	3	36	36(Kr)
$Fe(CO)_2(NO)_2$	26	4	6	36	36(Kr)
$Fe(NO)_2(PR_3)_2$	26	4	6	36	36(Kr)

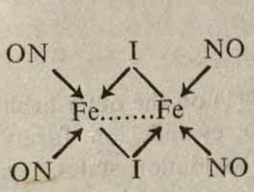
Recall the structure of NO from Chapters 5 and 18. The neutral molecule loses one electron and goes over to NO^+. This electron is transferred to the central transition metal ion whereby its valence is reduced by one unit. On the valence bond model the following resonating structures are suggested, which allow double bonding between the metal ion and the nitrogen:

$$\mathrm{M} + :\dot{\mathrm{N}}\underset{\cdot\cdot}{::}\mathrm{O}: \rightarrow \dot{\mathrm{M}}^- + :\mathrm{N}\underset{\cdot\cdot}{::}\mathrm{O}:^+ \rightarrow \dot{\mathrm{M}}^-:\mathrm{N}\underset{\cdot\cdot}{::}\mathrm{O}:^+ \longleftrightarrow \dot{\mathrm{M}}^{\times}_{\times}\,:\mathrm{N}:\ :\ddot{\mathrm{O}}:$$

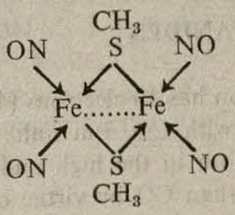
$$\left(\mathrm{M} + \mathrm{N}\underset{=}{\leftarrow}\mathrm{O}\right) \rightarrow \left(\mathrm{M}^- + \mathrm{N}\underset{\rightleftharpoons}{\leftarrow}\mathrm{O}^+\right) \rightarrow \left(\mathrm{M}^-\leftarrow\mathrm{N}\underset{=}{\leftarrow}\mathrm{O}^+\right) \longleftrightarrow \left(\mathrm{M}^- = \mathrm{N} = \mathrm{O}^+\right)$$

On the molecular orbital model one sp_x hybrid orbital of NO^+ containing the lone pair overlaps with a suitable metal orbital (sp^3 or d^2sp^3) forming the sigma bond from nitrogen to the metal. Since oxygen is more electronegative than nitrogen, it is the nitrogen that links to the metal. Just as in CO, we have in NO^+ one bonding σsp_x M. O. between nitrogen and oxygen. The corresponding σsp_x^* antibonding M. O. being of higher energy is not available for overlap by the back-donated electrons from the metal. The πp_y^* and πp_z^* antibonding M. O.'s of NO^+ are empty and can overlap with filled metal d-orbitals (d_{xy}, d_{xz}, d_{yz} orbitals in octahedral case and $d_{x^2-y^2}$ and d_{z^2} for the tetrahedral case).

The nitrosyl halides and Roussin's salts are dimers with metal—metal bonds:



(23-I)



(23-II)

Diamagnetism of these compounds can be explained on the basis of an Fe—Fe bond whereby the krypton shell is attained ($26+3\times2+2+1+1 = 36$).

Structural studies show that the metal-nitrogen bond in nitrosyls is extremely short indicating substantial double bonding. In metal carbonyls all M—C distances are in the range 1.7—1.9A and all M—N distances in metal nitrosyls are around 1.57—1.67A.

An interesting nitrosyl complex is the brown ring compound encountered in qualitative detection of nitrates. The compound usually formulated as $FeSO_4 \cdot NO$ is really $[Fe(NO)(H_2O)_5]SO_4$ in aqueous acid solution. The magnetic moment is ~ 3.9 B.M. indicating three unpaired spins (μspin only = 3.89 B.M.). This fits well with a monovalent iron complex. If NO transfers one electron it becomes NO^+ so that iron has to be unipositive to balance the charge of the binegative sulphate ion. Similarly in nitroprusside $Na_2[Fe(CN)_5NO]$, NO is taken as unipositive, two sodium ions are also unipositive so that iron has to be bipositive in order to balance the five negative CN groups.

23.3.3. Bent Nitrosyls: $[Ir(CO)Cl(PPh_3)_2\ (NO)]^+$ and $[Co\ (en)_2Cl(NO)]^+$ are good examples; the M—N—O angles are 124° and 121° respectively. The bond angle is suggestive of the fact that the nitrogen atom is sp^2 hybridised. The π^* antibonding M. O. of NO^+ is empty. In the bent nitrosyls it is considered that a paired set of electrons from a filled d-orbital of the metal is transferred to the NO^+ making this effectively NO^-. The nitrogen of NO^- is considered to be sp^2 hybridised. Of the three sp^2 hybrid orbitals two house two lone pairs and the third an unpaired electron. The third p orbital (outside sp^2) carries another electron. The nitrogen is bonded to oxygen by a double bond utilising the sp^2 electron and the p electron of the nitrogen. One lone pair of nitrogen is coordinated to the metal and the other lone pair remains as it is. Conversion of a linear nitrosyl complex to a bent nitrosyl complex results from an intramolecular transfer of an electron pair from the metal to the ligand (Fig. 23.4).

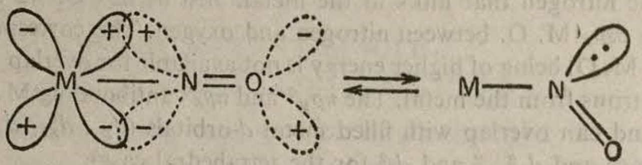


FIG 23.4. Change of a linear nitrosyl complex to a bent nitrosyl complex

23.4. METAL CYANIDES

The cyanide ion has 10 electrons (4+5+1) on the outer orbitals, and is therefore isoelectronic with CO. But unlike CO, cyanide ion forms extensive series of compounds both in the high and low oxidation states. Cyanide is a much stronger σ donor than CO by virtue of its negative charge and by virtue of its linking to a somewhat less electronegative element nitrogen (compared to oxygen of CO). It is a weaker π-acceptor than CO. It forms hexacyano, pentacyano, tetracyano and dicyano complexes:

I. Hexacyano Complexes: $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]$, $K_3[Mn(CN)_6]$, $K_3[Co(CN)_6]$ etc.

II. Pentacyano Complexes: $K_2[Fe(CN)_5NO]$, $K_4[Co(CN)_5(S_2O_3)]$ etc.

III. Tetracyano Complexes: $K_2[Ni(CN)_4]$, $K_2[Zn(CN)_4]$ etc.

IV. Dicyano Complexes: $[Co(en)_2(CN)_2]X$, $[Co(BigH)_2(CN)_2]X$

Cyano complexes are generally prepapred by the action of KCN on aquo metal complexes or other suitable complexes. Thus action of KCN on aqueous $FeSO_4$ gives $K_4[Fe(CN)_6]$. Similar action on $[Co(BigH)_3]X_3$ gives $[Co(BigH)_2(CN)_2]X$. $[Co(S_2O_3)(NH_3)_5]X$ reacts with KCN to produce $K_4[Co(S_2O_3)(CN)_5]$ etc. In all these cases cyanide ion functions as a monodentate ligand through carbon.

It should be noted that CN^- is capable of serving as a bridging ligand by utilising its lone pairs on carbon as well as on nitrogen. This behaviour is noted in polymeric AuCN, $Zn(CN)_2$, $K[Cu(CN)_2]$ (29-VI). Cyano complexes are of varied stereochemical configurations (linear in $[Ag(CN)_2]^-$; equilateral triangular in $[Cu(CN)_2]_n^{n-}$ (29-VI); regular tetrahedral in $[Zn(CN)_4]^{2-}$; octahedral in $[Co(CN)_6]^{3-}$). The nitrogen of the cyano group may also be utilised for coordination to Lewis acids. Thus $K_4[Fe(CN)_6]$ slowly absorbs six molecules of BF_3 while $[Fe(o\text{-}phen)_2(CN)_2]$ absorbs two molecules of BF_3. The lone pair on the nitrogen atom of the cyanide ion is linked to boron.

It is interesting to note that although cyanide ion has strong reducing properties, low-valent metal cyanides are rather less stable. This may be mis-understood to be an indication of its weaker π-acceptor property but it should also be noted that compared to the carbonyls, isocyanides or the phosphines the cyano complexes are all much too negatively charged, as for example the zero-valent nickel cyanide complex: $K_4[Ni(CN)_4]$.

The short metal-carbon bonds in metal cyanides can be accounted for on the valence bond model by the following resonating structures:

$$\mathrm{M}:\mathrm{C}\vdots\vdots\,\mathrm{N}:^- \longleftrightarrow \mathrm{M}^{\times}_{\times}:\mathrm{C}::\ddot{\mathrm{N}}:^-$$

$$(\mathrm{M} \leftarrow \mathrm{C} \overset{\leftarrow}{\equiv} \mathrm{N}^-) \longleftrightarrow (\mathrm{M} = \mathrm{C} = \mathrm{N}^-)$$

On the molecular orbital approach the carbon sp_x hybrid with the lone pair overlaps with a suitable hybrid orbital of the metal (dsp^2 or d^2sp^3). Suitable filled metal orbitals overlap with empty antibonding π^* orbitals of CN^- (π^*p_y or π^*p_z M.O.). Incidentally cyanide ion is the strongest coordinating ligand known (Chapter 10).

Because of its very high crystal field strength all cyano complexes are low spin eg: $K_4[Fe(CN)_6]$, $3d^6$; t^6_{2g}; diamagnetic; $K_3[Fe(CN)_6]$, $3d^5$; t^5_{2g}; 1.73 B.M.; $K_3[Mn(CN)_6]$, d^4; t^4_{2g}; 2.83 B.M.

23.5. METAL ISOCYANIDES (ISONITRILES)

Alkyl- and aryl-isocyanides ($C = N-R$) give metal complexes in low as well as in common oxidation states. An isocyanide has a lone pair on carbon to serve as a σ-donor as also a π^* M.O. on carbon and nitrogen to serve as an acceptor.

23.5.1. Syntheses and Reactions: Isocyanides are commonly obtained by the reaction of a transition metal cyanide (eg: AgCN) with alkylating agents:

$$AgCN + CH_3Cl \rightarrow AgCl + CNCH_3$$

Tetrakis (aryl-isocyanido) nickel (0) is obtained by the action of excess CNR on $Ni(CO)_4$. Bis (dimethylglyoximato) nickel (II) has also been reduced in presence of CNR by hydrazine:

$$Ni(CO)_4 + 4CNR \rightarrow Ni(CNR)_4 + 4CO$$

$$2Ni(DMG)_2 + 8CNR + N_2H_4 \rightarrow 2Ni(CNR)_4 + 4DMGH + N_2$$

$[Ni(CNR)_4]$ forms diamagnetic ($3d^{10}$) yellow crystals which are stable to air and are soluble in organic solvents.

An alcoholic suspension of chromium (II) acetate reacts with aryl-isocyanide to give a lively disproportionation reaction of chromium (II) to chromium (III) and chromium (o):

$$3Cr^{2+} + 18CNR \rightarrow [Cr(CNR)_6] + 2[Cr(CNR)_6]^{3+}$$

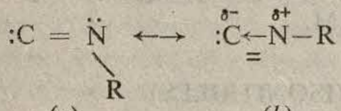
The hexakis (isocyanido) chromium (III) salts could not be isolated but the yield of the $[Cr(CNR)_6]$ agrees with the above equation. The hexakis (isocyanido) chromium (0) compounds form yellow to red diamagnetic low spin (t^6_{2g}) crystals. They are stable to air and are soluble in chloroform and benzene and sparingly soluble in alcohol.

Reaction of CoX_2 and CNR gives green coloured crystals of empirical composition $CoX_2(CNR)_2$. Conductivity suggests an ionic formulation $[Co(CNR)_4]$ $[CoX_4]$ (X = Cl, Br, SCN; $R = CH_3$). A series of blue-violet coloured CoX_2 $(CNR)_4$ (X = Cl, Br; $R = CH_3$) have also been synthesised. They show one unpaired spin and behave as bi-univalent electrolytes so that they have been formulated as square planar $[Co(CNR)_4]X_2$. Hydrazine reduces them to yellow-brown, diamagnetic cobalt (I) derivatives:

$$5Co(CNR)_4I_2 + N_2H_4 \rightarrow 4[Co(CNR)_5]I + CoI_2 + 4HI + N_2$$

Manganese (I) complexes are discussed in Chapter 27.

23.5.2. Structure and Bonding: Two resonating structures can be written for CNR:



(*a*) (*b*)

Structure (*a*) has sp^2 hybridised nitrogen. This structure indicates a C−N−R bond angle ~ 120° i.e. CNR should be a bent molecule. But structure (*b*) admits of a linear C−N−R. Resonance between the two forms (*a*) and (*b*) would be favoured only with a linear or nearly linear geometry. (If structure (*a*) is to be linear both the carbon and nitrogen have to be *sp* hybridised). Structural studies on $[Co(CNCH_3)_5]^+$ show that Co−C−N−C is linear, thus supporting the structure (*b*). The Co−C distance (1.87A) is significantly shorter than Co−C single bond (~ 2.07A) indicating back donation to CN π^* orbital from $d\pi$ orbitals of cobalt. CN− part of CNR is isoelectronic with CO and CN^- (cyanide ion) so that we can picture a similar M.O. distribution for CNR as for CO.

Compared to CO, CNR is evidently a better σ donor as is shown by the formation of complexes of cobalt (II), chromium (III), manganese (II), iron (II) etc. Corresponding complexes with CO are unknown. That CNR is a weaker π-acceptor is shown by the following reaction:

$$Co_2(CO)_8 + 5CNR \rightarrow [Co(CNR)_5] [Co(CO)_4] + 4CO$$

That $[Co(CNR)_5]^+$ is indeed the cation is shown by the reaction:

$$Na[Co(CO)_4] + [Co(CNR)_5]ClO_4 \rightarrow [Co(CNR)_5][Co(CO)_4] + NaClO_4$$

CO prefers the lower oxidation state -1 to $+1$.

It should be noted that while carbon in CO is linked to a strongly electronegative oxygen, carbon in CNR is linked to a lesser electronegative nitrogen. Therefore lone pair in CO is less readily donated to a metal for σ bond formation while the lone pair of carbon in CNR is rather more responsive. For the presence of more electronegative oxygen CO becomes a better π acceptor whereas due to the presence of a less electronegative nitrogen CNR shows poorer π acceptor properties.

23.6. COMPLEXES WITH TRIVALENT PHOSPHORUS AND ARSENIC LIGANDS

Trivalent phosphorus and arsenic compounds such as PX_3, AsX_3 can not only serve as donors by virtue of their lone pairs but can also serve as acceptors because they possess empty *d*-orbitals as well. Corresponding NX_3 compounds can function only as donors but not as acceptors since they do not have any low energy *d*-orbitals. The sp^3 hybrid orbital of the tetrahedral phosphorus or arsenic with the lone pair overlaps with a suitable metal hybrid orbital (sp^3, dsp^2 or d^2sp^3) to form the sigma metal phosphorus or sigma metal-arsenic bond. Then suitable filled metal *d*-orbitals overlap with an empty *d*-orbital of the phosphorus or arsenic (Fig. 23.5).

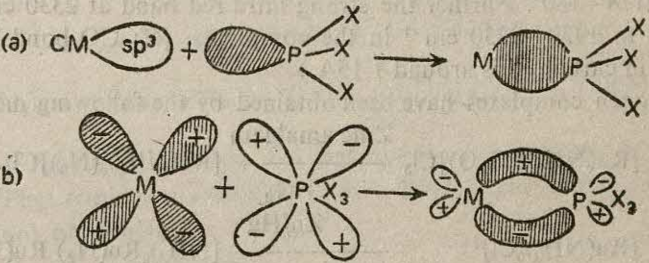


FIG. 23.5. Bonding in metal—PX_3 compounds
(*a*) metal phosphorus sigma bond
(*b*) metal-phosphorus π-bond

Some low valent metal complexes with trivalent phosphorus and arsenic ligands are: $[Ni(PCl_3)_4]$, $[Ni(PF_3)_4]$, $[Fe(CO)_3(PPh_3)_2]$, $[Mo(CO)_3(AsCl_3)_3]$, $[Cr(CO)_2(diars)_2]$ etc.

23.7. MOLECULAR NITROGEN COMPLEXES

Molecular nitrogen is isoelectronic with carbon monoxide. Both have an effective triple bond and a lone pair of electrons on each of the two atoms. Oxygen orbitals being more stable than those of carbon the bonding orbitals of CO have more oxygen character while the antibonding orbitals have more carbon character. Bonding orbitals of N_2 are little more stable than the bonding orbitals of CO while the antibonding orbitals are less stable. The energies of the two atomic orbitals of the two nitrogen atoms are the same. Thus N_2 is a weaker σ donor as well as a weaker π-acceptor than carbon monoxide. That N_2 is a weaker σ donor than carbon of CO follows from higher electronegativity of nitrogen,

Molecular nitrogen complexes are known in 0, +1 and +2 oxidation states while carbonyl complexes are known with the metal ion in −2, −1, 0 and +1 oxidation states.

Some examples are $[W(N_2)_2(PMe_2\phi)_4]$ (yellow), $[Co(N_2)(P\phi_3)_3]$ (red), $[IrCl(N_2)P\phi_3)_2]$(yellow), $[Ru(NH_3)_5(N_2)]^{2+}$ (pale yellow), (*cis*) $[Ru(N_2)_2(en)_2]^{2+}$ (pale yellow) etc.

Carbon monoxide participates in both homo- and mixed ligand complexes while dinitrogen is known to exist as a donor in mixed ligand complexes only.

Carbon monoxide functions both as a terminal monodentate ligand and also as a ketonic bridge (carbon being sp^2 hybridised) in polynuclear carbonyls (eg: $(OC)_3\,Co(-\overset{O}{C}-)\,(-\overset{O}{C}-)\,Co(CO)_3]$. The oxygen lone pair does not participate in bridging. On the contrary dinitrogen functions both as a terminal ligand and as an end−on bridging ligand (eg: $[(NH_3)_5\,Ru \leftarrow N \equiv N - \rightarrow Ru(NH_3)_5]^{4+}$). Molecular nitrogen complexes are much less stable than the metal carbonyls.

Nitrogen−nitrogen distance in N_2 is 1.097A while the corresponding distances in $[Ru(NH_3)_5N_2]Cl_2$ and $[(NH_3)_5\,Ru(N_2)\,Ru(NH_3)_5[\,(B\phi_4)_4$ are 1.12A and 1.124A. The linearity of the MNN bond angle is shown by the fact that in all complexes $<MNN \simeq 178-180°$. Further the strong infra red band at 2330 cm^{-1} of free N_2 goes down to 1930−2230 cm^{-1} in the complexes. (cf: CO bond length is 1.13A while that in carbonyls is around 1.15A.)

Dinitrogen complexes have been obtained by the following methods:

1. (*a*) $[Ru(NH_3)_5(H_2O)]Cl_3 \xrightarrow[+N_2]{\text{Zinc amalgam}} [Ru(NH_3)_5(N_2)]Cl_2$

   (*b*) $[Ru(NH_3)_5Cl]^{2+} \xrightarrow[N_2]{Zn/Hg} [NH_3)_5Ru(N_2)\,Ru(NH_3)_5]^{4+}$

2. $[Ru(NH_3)_5(H_2O)]^{3+} \xrightarrow{\text{aq. } N_2H_4} [Ru(NH_3)_5(N_2)]^{2+}$

Chatt and coworkers reported 88% yield for the preparation of *trans* $[Mo(N_2)_2(dppe)_2]$ (dppe = diphenyl-phosphino ethane) from $MoCl_3\,(thf)_3$ (thf = thenoyl trifluoroacetone) and Na/Hg in the pressnce of dppe and N_2 with a three hour reaction time. The overall pathway is:

$$\begin{tikzcd}
MoCl_5 \arrow[r, "EtCN", "reflux"'] & MoCl_4\,(Et\,CN)_2 \arrow[d, "\begin{array}{l}Zn\\ CH_2Cl_2/thf\end{array}"] \\
\textit{trans}\ Mo(N_2)_2\,(dppe)_2 & MoCl_3\,(thf)_3 \arrow[l, "Na/Hg"', "dppe/N_2"]
\end{tikzcd}$$

The compound has a centrosymmeture structure. Mo—N length of 2.01A is comparable to Mo—N single bond length while the N—N distance of 1.1A does not differ significantly from that in free N_2.

It is observed that heavier transition metals form more dinitrogen complexes than lighter elements. It is likely to be prompted by the better π-donor ability of the heavier elements because of increasing electropositive character down any periodic group. Better π-donation to dinitrogen makes it a better base while remaining coordinated to a metal. The nature of δ donation from N_2 to M and π back donation from M to N_2 is parallel to that in metal carbonyls.

Poor complexing property of molecular nitrogen has been, however, a real boon to organic chemists and organometallic chemists in that many synthetic reactions can be carried out using nitrogen as the inert medium. Coordination chemists are now trying to reduce the coordinated nitrogen to ammonia so that a method for fixation of atmospheric nitrogen may be invented through the catalytic participation of a suitable metal ion.

Direct reduction of N_2 to NH_3 (or NH_4^+) involves as many as six electrons which are expected to come from the metal:

$$M^\circ \leftarrow N \equiv N \xrightarrow[-6e]{6H^+} M^{6+} + 2NH_3$$

This is difficult to accomplish. Certian phosphine complexes of molybdenum and tungsten containing dinitrogen, however, readily yield ammonia in acidic medium:

(*a*) $[MoCl_3(thf)_3] + 3e + 2N_2 + \text{excess dppe} \rightarrow [Mo(N_2)(dppe)_2] + 3Cl^-$

$[Mo(N_2)_{2\,(Dppe)_2}] + 6H^+ \rightarrow 2NH_4^+ + N_2 + Mo^{VI}$ products

(*b*) $2[Mo(N_2)_2\ (triphos)\ (PPh_3)] + 8HBr\text{-} \xrightarrow[thf]{} 2NH_4Br + 3N_2 + 2PPh_3 + \underset{(triphos)}{2MoBr_3}$

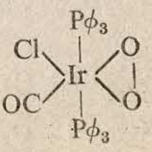
[thf = tetrahydrofuran; dppe = diphenylphosphinoethane, $Ph_2P—CH_2—CH_2—PPh_2$; triphos = $PhP(CH_2—CH_2—PPh_2)_2$, phenyl bis (ethyldiphenyl phosphino) phosphine]

23.8. MOLECULAR OXYGEN COMPLEXES

In chemical reactions oxygen usually acts as an oxidising agent. Such reactions are called oxidation. Since 1963, however, many synthetic reactions have come to light where the O_2 molecule i.e. the dioxygen remains coordinated to a metal ion. Such reactions have been termed oxygenation.

Dioxygenation coordination chemistry started with Vaska's discovery of the reaction of O_2 on *trans* Ir $(P\phi_3)_2(CO)Cl$:

trans Ir $(P\phi_3)_2(CO)Cl + O_2 \rightleftharpoons$



Preparation: The majority of metal—dioxygen complexes are formed by reaction of gaseous molecular oxygen with d^7, d^8 or d^{10} complexes in solution. The reactions may be classified as under:

1. No reaction: $Rh(P\phi_3)_2(CO)Cl \xrightarrow{O_2}$ no reaction

2. Formation of a mononuclear dioxygen adduct with or without displacement of ligands:

$$Ir(P\phi_3)_2(CO)Cl \xrightarrow{O_2} Ir(P\phi_3)_2(CO)Cl(O_2)$$

$$Co(DMG)_2 \xrightarrow[\text{pyridine}]{O_2} Co(DMG)_2\ (\text{pyridine})\ (O_2)$$

DMG stands for the dimethylglyoximate anion.

3. Formation of a dimer or a binuclear dioxygen adduct

$$2Rh(P\phi_3)_3Cl \xrightarrow{O_2} [Rh(P\phi_3)_2(O_2)Cl]_2$$

$$2\ Co(\text{histidinate})_2 \xrightarrow{O_2} Co_2\ (\text{histidinate})_4\ (O_2)$$

4. Oxidation of ligands with the oxidised ligand remaining coordinated:

$$Ru(P\phi_3)_2(CO)_2(SO_2) \xrightarrow{O_2} Ru(P\phi_3)_2(CO)_2(SO_4)$$

5. Displacement of free oxidised ligand:

$$Pt(P\phi_3)_4 \xrightarrow{2O_2} Pt(P\phi_3)_2(O_2) + 2\phi_3PO$$

Group VIII d^{10} complexes (Ni(o). Pd(o), Pt(o)) generally react with molecular oxygen giving 1:1 adducts with ligand displacement and/or oxidised ligand. In general reactivity with molecular oxygen increases in going from second row to third row : Os(o) > Ru(o); Ir(I) > Rh(I). For complexes of the same metal reactivity is increased by strong σ donor ligands such as phosphine and by polarisable ligands. Partial or total deactivation is caused by strong π acceptor ligands such as CO and electronegative ligands or a positive charge on the complex.

$$Ir(P\phi_3)_2(CO)Cl \xrightarrow{O_2} Ir(P\phi_3)_2(CO)Cl(O_2)$$

$$Ir(P\phi_3)_3Cl + O_2 \xrightarrow{\text{very fast}} Ir(P\phi_3)_2Cl(O_2)$$

$$[Ir(P\phi_3)_2(NO)Cl] + O_2 \longrightarrow \text{no reaction}$$

Reactions of coordinated dioxygen: Dioxygen complexes have been observed to react with aqueous acid to give H_2O_2, with reducing agents to give coordinatively unsaturated complexes and with various ligands which displace molecular oxygen. Apart from these reactions, however, there is a class of reactions that appears to involve oxidation of substrates by dioxygen in the coordination sphere of the metal. Under mild conditions without catalyst molecular oxygen does not react with SO_2, CO_2, CS_2, CO, NO_2, alkyl isocyanides, ketones, aldehydes or triphenylphosphine. Dioxygen complexes of Group VIII transition metals, however, do react with all of these substrates to form complexes of the oxidised substrates:

$$ML_2(O_2) \xrightarrow{SO_2} ML_2(SO_4);$$
$$(M = Pd, Pt;\ L = P\phi_3, As\phi_3)$$

$$Ir(P\phi_3)_2(CO)X(O_2) \xrightarrow{SO_2} Ir(P\phi_3)_2(CO)X(SO_4)$$
$$(X = Cl, Br, I, NO_3, -C \equiv CR)$$

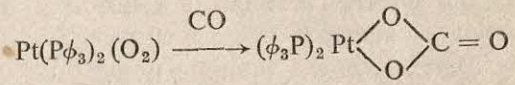
$$Ir(As\phi_3)_2(CO)X(O_2) \xrightarrow{SO_2} Ir(As\phi_3)_2(CO)X(SO_4)$$

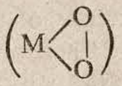
$$Ir(P\phi_3)_3Cl(O_2) \xrightarrow{SO_2} \xrightarrow{CO} Ir(P\phi_3)_2(CO)Cl(SO_4)$$

$$RhLCl(O_2) \xrightarrow{SO_2} RhLCl(SO_4)$$

$$M(P\phi_3)_2(O_2) \xrightarrow{NO_2} M(P\phi_3)_2(NO_3)_2;\ (M = Pd, Pt)$$

$$IrL_2(CO)X(O_2) \xrightarrow{NO_2} IrL_2(CO)X(NO_3)_2$$



There are three possible explanations for the increase in reactivity of dioxygen upon coordination: (1) coordinated dioxygen  is in general diamagnetic; therefore reactions with diamagnetic substrates to form diamagnetic products are not hindered by the requirement of spin conservation (2) the metal may hold the dioxygen and the substrate in *cis* positions, lowering the activation energy for oxidation of the substrate (3) coordinated dioxygen is, in most cases, partially reduced; increased electron density on the dioxygen may activate it. In most cases the metal is in a low oxidation state (+1 or 0) and this is likely to enhance the electron density on the coordinated dioxygen.

Nature of the Bonding: A. The dioxygen molecule: The valence orbitals of the two oxygen atoms ($2s^22p^4$) combine to give molecular orbitals whose relative energies are shown in Fig. 23.6. The ground state of molecular oxygen is predicted and observed to be a triplet state with two unpaired electrons occupying a pair of degenerate π^* antibonding orbitals. The lowest excited states are formed by redistributing the two electrons in these $2p\pi^*$ antibonding orbitals. M. O. theory predicts bond orders of 2.5, 2, 1.5 and 1 for the dioxygenyl cation O_2^+, dioxygen O_2, superoxide ion O_2^- and peroxide O_2^{2-} ion respectively.

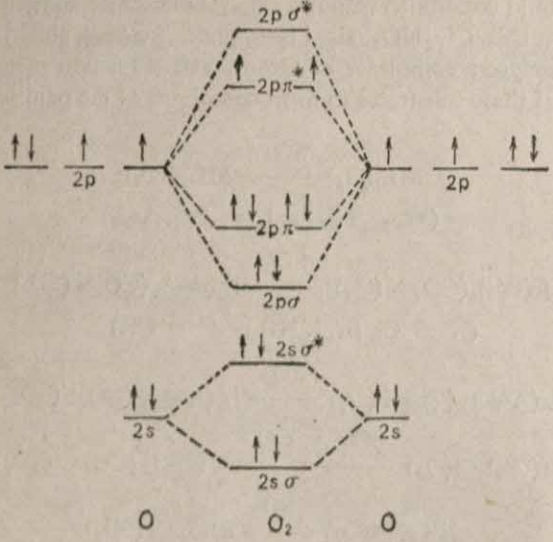
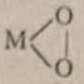


FIG. 23.6. M. O. diagram of dioxygen

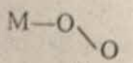
Species	Example	O–O distance	O–O bond order
O_2^+	O_2PtF_6	1.12A	2.5
O_2	—	1.21	2
O_2^-	KO_2	1.28	1.5
O_2^{2-}	H_2O_2	1.49	1

The bond dissociation energies of O_2^+, O_2, O_2^-, and O_2^{2-} are 149, 118, 84 and 49 Kcal/mole respectively. These values nicely follow the bond order calculated from the M. O. theory (Part I ; p. 104).

B. Structure and Bonding in metal Complexes: Two different classes of 1:1 bonding of the dioxygen ligand to transition metal complexes have been demonstrated. Class I compounds are diamagnetic 1:1 adducts of dioxygen with organo-metallic group VIII transition metal complexes in which the O–O bond remains intact but is longer than in free O_2 and the two M–O distances are equal. All diamagnetic mononuclear dioxygen complexes consist of triangular structures in which the two oxygen atoms are equivalently bonded to the metal. The O–O bond lengths in these complexes vary over a wide range 1.31A



I
common type



II
uncommon type

to 1.66A depending on the electron density at the central atom, which is strongly influenced by the other ligands.

The bonding of metals to O_2 in configuration I can be described by analogy to the description of acetylene—metal complexes or ethylene–metal complexes. Both π and π^* orbitals of molecular oxygen have proper symmetry to interact with the bonding set of metal s, p and d orbitals. Conceptually a μ bond is formed by transfer of electron density from a filled dioxygen π bonding orbital to s, p and d orbitals of appropriate symmetry (eg: dsp^2, d^2sp^3) on the metal and one π bond is formed by transfer of electron density from one filled metal d orbitals into an empty π^* orbital of dioxygen. In order to have such an overlap the two unpaired electrons residing in the two π^* M. O. of O_2 molecule must move into one orbital and thus pair their spins and give rise to diamagnetic chelates. For example, in the case of a d^{10} system it is most likely that one of the two unpaired electrons in one of the two orbitals of dioxygen will move into one particular π^* orbital, thus making the other π^* orbital available for back overlap with a filled d orbital of the metal. However in the case of d^8 system there are two metal orbitals each with one unpaired electron. If the d^8 metal ion forms an outer orbital sp^3d^2 complex then the two metal orbitals with one unpaired electron each may overlap the two half filled π^* orbitals of dioxygen, thus making the resulting complex diamagnetic. Depending on the hybrid orbitals of the central metal atom (say dsp^2, dsp^3) usually one inner d orbital is reserved for hybridisation. Then eight electrons are accommodated in the remaining four d orbitals giving diamagnetic complexes. d orbitals of different quantum shells may have to be used for forward and back bonding (eg. d^{10}). It should be noted that while peroxide occupies two coordination positions neutral dioxygen, ethylene, on the other hand formally occupy only one as represented below:

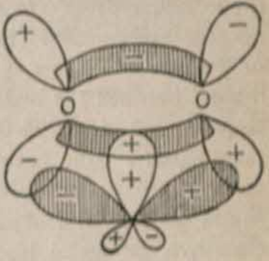
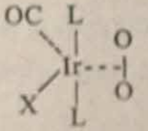


FIG. 23.7.
Bonding in class I dioxygen metal complexes.



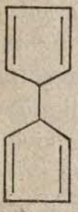
L	X	O—O(A)
$P\phi_3$	Cl	1.30 ± 0.03
$P\phi_3$	Br	1.36 ± 0.03
$P\phi_3$	I	1.509 ± 0.026
$P\phi_2Et$	Cl	1.461 ± 0.014

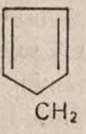
There is significant difference in the nature of bonding in CO, N_2 complexes on the one hand and dioxygen on the other. There is no σ type lone pair (as in CO, N_2) available for bonding in dioxygen. In dioxygen complexes both the orbitals of dioxygen are of the π type. This is because Pauling's V. B. model is not valid for O_2 as it is found to be paramagnetic (= 2 unpaired spins). The filled $p\sigma$ bond in oxygen is shielded by two $p\pi$ bonding M. O.'s and hence cannot be reached by any metal sigma orbitals.

23.9. SANDWICH COMPOUNDS: METALLOCENES AND METAL ARENES

23.9.1. The Beginning: Two distinct classes of ligands exist: (1) those with lone pairs of electrons as in the classical Werner complexes and (2) those without lone pairs but having only π-electrons as in the non-classical organometallics (page 202. Part I). *Organometallic complexes are those in which there is bonding between carbon atom (s) of the ligand and the metal.* Organometallic complexes may again be of two types: (*a*) σ-type organometallics in which there is only a σ-bond between the metal and carbon, the electron density being symmetrically concentrated along M-C internuclear axis; (*b*) π-type organometallics in which there exists π-bond between the metal and the ligand. In the latter type one or more double or multiple bond π-electrons participate significantly in the bonding. Metal carbonyls, isocyanides may be designated as organometallics. In metal carbonyls or metal isocyanides the metal is linear with the bond axis of CO, $-$CNR etc. On the contrary, in metallocenes or metal arenes, both the forward L→M donation and the M→L back donation are accomplished through π-orbitals of the ligands. As a consequence the metal cannot lie linearly with the ligand—instead it has to stay away from the molecular plane of the ligand.

In 1951 two groups of chemists accidentally made a break-through in our very ideas of coordination. Kealy and Pauson attempted synthesis of dihydrofulvalene (dicyclopentadienyl), $C_5H_5-C_5H_5$ (23-III), by oxidation of cyclopentadiene C_5H_6 (23-IV), (taken in the form of cyclopentadienyl magnesium bromide C_5H_5MgBr) by $FeCl_3$ in ether solution. (The corresponding oxidation of phenylmagnesium bromide gives good yields of diphenyl). Instead of producing the desired material the experiment ended up in a stable orange coloured compound which analysed as $Fe(C_5H_5)_2$. Miller et al simultaneously obtained the same compound by passing cyclopentadiene vapour over an iron-molybdenum catalyst at ~300°C.


(23-III)


(23-IV)

$$6C_5H_5MgBr + 2FeCl_3 \rightarrow 3C_5H_5-C_5H_5 + 2Fe + 3MgBr_2 + 3MgCl_2 \text{(planned reaction)}$$

$$2C_5H_5MgBr + FeCl_2 \rightarrow (C_5H_5)_2Fe + MgBr_2 + MgCl_2 \text{(actual reaction)}$$

$$2C_5H_6 + Fe \rightarrow (C_5H_5)_2Fe + H_2$$

Intense activities followed in U.S.A. and in Germany. Structure of $Fe(C_5H_5)_2$ was soon established as centrosymmetric with the iron sandwiched between the two cyclopentadiene rings.

In recognition of the aromatic character of the $Fe(C_5H_5)_2$ complex it was named ferrocene. Ferrocene was the fore runner of a whole field of non-Werner π-aromatic complexes, many hundreds of which are now known and still newer ones are being synthesised every year.

23.9.2 Metallocenes: Strong electropositive metals only give ionic cyclopentadienides. These are readily decomposed by solvents which are stronger acids than cyclopentadienes:

$$Na+C_5H_6 \rightarrow NaC_5H_5+\tfrac{1}{2}H_2\ ;\ NaC_5H_5+H_2O \rightarrow NaOH+C_5H_6$$

π-type sandwich covalent complexes are given by all first transition series metals with the exception of Mn(II) and Cu(II). Mo(II), W(II), U(IV), Rh(II), Rh(III), Ir (III) of the later series give π-type sandwich complexes. Evidences indicate that in $[Mn(C_5H_5)_2]$ there is not much covalent overlap with the π-electrons of the two rings and manganese (II) electrons; instead there is a localised C-Mn-C σ-bond. A representative list of π-cyclopentadienyls of transition metals is given in Table 23.4.A fascinating *triple deck sandwich* complex $[(C_5H_5)^- Ni^{2+} (C_5H_5)^- Ni^{2+} (C_5H_5)^-]\ BF_4$ has also been established.

Syntheses: 1. Interaction of cyclopentadienyl magnesium halide in ether with an ether-soluble metal salt or a metal complex:

$$2C_5H_5MgBr+MX_2 \rightarrow (C_5H_5)_2M+2MgBrX$$

$$2C_5H_5MgBr+M(acac)_2 \rightarrow (C_5H_5)_2M+MgBr_2+Mg(acac)_2$$

Table 23.4. Some Metal Cyclopentadienyls*

Group	IV	V	VI	VII	VIII		
First Transition series	$[Cp_2Ti]_2$ green	$[Cp_2V]$ violet	$[Cp_2Cr]^+$ yellow	Mn^{2+}	$[Cp_2Fe]^+$, blue	$[Cp_2Co]^+$, yellow	$[Cp_2Ni]^+$ yellow
		$[Cp_2V]^+$ purple	$[Cp_2Cr]$ red		$[Cp_2Fe]$, orange	$[Cp_2Co]$, purple	$[Cp_2Ni]$ green
		$[Cp_2V]^{2+}$ green					
Second Transition series	$[Cp_2Zr]_n$	$[Cp_2Nb]^{3+}$ red-brown	$[Cp_2MoH_2]$ yellow		$[Cp_2Ru]$, yellow	$[Cp_2Rh]^+$ colourless	
Third Transition series		$[Cp_2Ta]^{3+}$ rose	$[Cp_2WH_2]$ yellow		$[Cp_2Os]$, colourless	$[Cp_2Ir]^+$, colourless	$[Cp_4Pt_2]$ dark green

*Cp^- = cyclopentadienyl anion. In order to specify the number of carbon atoms that are linked to a metal atom Cotton has introduced '*hapto*' prefix. Thus $(C_5H_5)_2Fe$ is called bis (pentahaptocyclopentadienyl) iron, $(h^5-C_5H_5)_2Fe$, indicating that all the five carbon atoms are attached to iron. The symbol *h* has since been changed to η. The Greek word 'haptein' means 'to fasten'.

2. Interaction of Metal halides and cyclopentadiene: Bases such as trimethylamine, diethylamine or pyridine are used during these syntheses in order to arrest the liberated acid:

$$2C_5H_6+FeCl_2+2py \rightarrow [(C_5H_5)_2Fe]+2pyH.Cl$$

$$NiBr_2+2Et_2NH+2C_5H_6 \rightarrow [(C_5H_5)_2Ni]+2[Et_2NH_2]Br$$

The above synthesis of ferrocene is the basis of its commercial production.

3. Interaction of Metal Carbonyls and Cyclopentadiene:

$$M(CO)_x+2C_5H_6 \rightarrow [M(C_5H_5)_2]+xCO+H_2$$

4. Interaction of sodium cyclopentedienide and a transition metal halide:

$$2NaC_5H_5+CoCl_2 \xrightarrow{THF} [Co(C_5H_5)_2]+2NaCl$$

$$2NaC_5H_5+TiCl_4 \xrightarrow{THF} [TiCl_2(C_5H_5)_2]+2NaCl$$

Properties: *Ferrocene*, $[(C_5H_5)_2Fe]$ forms orange coloured crystals (M.P. 173–174°C). It is stable in air and can be sublimed. It is a non-electrolyte, is insoluble in water but soluble in organic solvents. It is diamagnetic. It can be oxidised by dilute HNO_3 as also by bromine or by electrolysis to the blue ferricinium cation, $[Fe(C_5H_5)_2]^+$. This is a 1:1 electrolyte, is soluble in water but insoluble in ether. This cation has one unpaired spin.

Cobaltocene, $[Co(C_5H_5)_2]$, has been obtained as deep violet-black needles (M.P. 173–174°C) by the action of sodium cyclopentadienide on $CoCl_2$ in THF or on $[Co(NH_3)_6](SCN)_2$ in liquid ammonia. This is air-sensitive and can be readily oxidised to the cobalticinium cation, $[Co(C_5H_5)_2]^+$. $[Co(C_5H_5)_2]$ is low-spin ($\mu \sim 1.76$ B.M.) while $[Co(C_5H_5)_2]Br$ is diamagnetic.

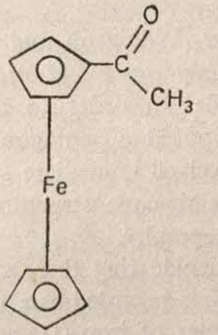
Nickelocene, $[Ni(C_5H_5)_2]$, has been obtained as dark emerald-green crystals (sublimes 80–90°C) by the action of C_5H_5MgBr on $[Ni(acac)_2]$ or on $[Ni(NH_3)_6](SCN)_2$ in liquid ammonia. It is readily soluble in organic solvents and is a non-electrolyte. It has the spin-only moment ($\mu \sim 2.86$ B.M.).

Aromatic Character and Aromaticity: Benzene is an unsaturated cyclic hydrocarbon. It has many peculiar chemical behaviours which make it so very different from open-chain unsaturated hydrocarbons. These special properties have led to the coinage of the term *aromatic* in respect of benzene and related derivatives. Some of these special properties are: (1) Unlike unsaturated, open-chain aliphatic compounds benzene and other aromatic compounds undergo substitution reactions rather than addition reactions. Thus bromination of benzene gives, for example, bromobenzene C_6H_5Br, instead of $C_6H_6Br_6$ via addition to the double bonds. (2) Benzene is extremely stable to oxidation eg: towards nitric acid or $KMnO_4$. Aliphatic unsaturated compounds undergo oxidation under these conditions. (3) Substituted benzene derivatives possess properties which are rather different from those of analogous aliphatic compounds. Aliphatic amines are far stronger bases than aromatic amines. Phenol is a stronger acid than alcohols- Acetic acid is weaker than benzoic acid. Aniline gives, in presence of HCl and $NaNO_2$, benzenediazonium chloride.

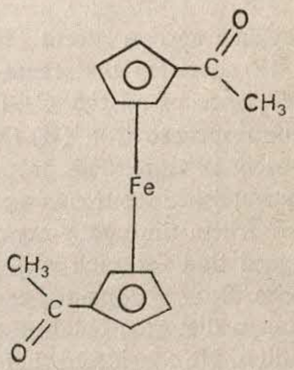
These special properties symbolised as *aromaticity* arise out of the special bonding in these compounds. In C_6H_6 aromatic ring all the six carbon atoms are sp^2 hybridised and each carbon atom has one electron in its p_z orbital. These p_z orbitals overlap to give rise to $\pi-$M.O.'s. The double bonds can resonate and thus the $\pi-p_z$ electrons are delocalised over the $\pi-$M.O. ring. In aliphatic unsaturated hydrocarbons like ethylene or other conjugated systems the double bonds are isolated and have no delocalisation energy. π-Electrons in benzene are under the influence of several nuclei and have thus greater bonding energy than the π-electrons of localised double bonds. Hence π-electrons are not available for addition reactions.

Huckel had shown that aromatic character should not be restricted only to benzene-like systems with 6π-electrons. In fact, all planar conjugated organic compounds with sp^2 hybridised atoms which have $4n+2$ ($n = 0, 1, 2, 3, 4$ or 5) π-electrons should exhibit aromaticity. The $C-C$, $C=C$, $C\equiv C$ distances in open-chain compounds show significant variation but carbon-carbon distance in all aromatic compounds have been found to be virtually constant at 1.39 ± 0.04A. This distance is so peculiar that it is now taken as a test of aromaticity.

Organic Reactions of Ferrocene: The stability of ferrocene in various reaction media was high enough to perform many organic substitution reactions without breakdown of the sandwich structure. Thus ferrocene reacts with acetyl chloride to furnish either acetylferrocene $CH_3COC_5H_4FeC_5H_5$ (23–V) or 1, 1′-diacetylferrocene $(CH_3COC_5H_4)_2Fe$ (23–VI). Reaction of ferrocene with n-butyl lithium in diethyl ether solution gives monolithium derivative $(LiC_5H_4)Fe(C_5H_5)$. Reaction of ferrocenyl-lithium with CO_2 followed by acidification gives ferrocenyl carboxylic acid $(C_5H_5)Fe(C_5H_4COOH)$. Ferrocene reacts in the presence of a sodium acetate buffer with $HgCl_2$ in methanol-ether solvent to give a mixture of golden yellow



(23–V)



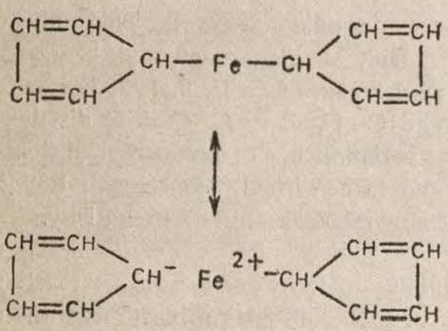
(23–VI)

ferrocenyl mercuric chloride, $(C_5H_5)Fe(C_5H_4HgCl)$ and yellow-brown 1, 1′-bis (chloromercuri) ferrocene $Fe(C_5H_4HgCl)_2$. Direct halogenation of ferrocene is not possible as under the reaction condition ferrocene undergoes oxidation to ferricinium ion which is then decomposed. However, ferrocenyl mercuric chloride reacts with N-halosuccinimides, $XN(CO)_2C_2H_4$ in dimethylformamide to give haloferrocenes $(C_5H_5)Fe(C_5H_4X)$.

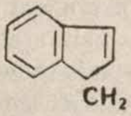
Because of so many diverse electrophilic substitution reactions ferrocene has been branded by Russian workers as *superaromatic*. In fact studies on the Friedel-crafts acylation reaction gives the following order of reactivity:

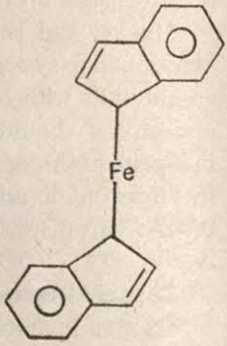
ferrocene > anisole > benzene

Structure and Bonding: Kealy and Pauson proposed the resonating structure (23-VII) which showed partial ionic bonding and localised σ-bonding of iron to



(23–VII)





(23–VIII)

the two methylenic carbon atoms. However, Wilkinson and coworkers soon showed from IR spectrum that there was only one C—H stretching frequency indicating equivalence of all the C—H bonds. In order to account for this equivalence with respect to iron (II) they proposed a pentagonal prism i.e. the so called sandwich structure. This proposal received immediate support from the simultaneously published centrosymmetric double-cone structure determined by Fischer and coworkers through X-ray crystallography.

Fischer argued that for each cyclopentadienide ring there are six (i.e. three pairs) π-electrons. Each cyclopentadienyl ion was regarded as a tridentate ligand, and ferrocene as a distorted octahedral complex of iron (II) with inner orbital d^2sp^3 hybridisation. He considered that the π-electrons had moved into the hybrid orbitals of iron (II). This point was apparently supported by the failure of hydrogenation of ferrocene under moderate conditions. Interestingly bis (indenyl) iron (II) (23-VIII) could be hydrogenated in the six membered ring to the extent of only four hydrogens per six-membered ring. The π-electrons of the double bond of the fused benzene ring were apparently (!) drawn into the cyclopentadiene fragment of the complex.

Fischer's view came in for sharp criticism by the Wilkinson group. Complete transfer of the ring π-electrons to the empty metal ion orbitals would fail to explain the aromatic nature of ferrocene. The carbon-carbon distance in ferrocene is 1.39 ± 0.04A which is typical of aromatic systems. If the π-electrons were drawn into metal orbitals their energies would be raised ($3d > 4s > 2p$) and hence ferrocene should fail to respond to aromatic character.

Ferrocene structure is now expressed on the basis of molecular orbitals. Symmetry permitted cyclopentadienyl ring orbitals are considered to overlap metal orbitals to form M.O.'s. Ring π-electrons and metal ion electrons are then fed into these M.O.'s in order of increasing energy. Electron spin-pairing or—unpairing is decided by the relative magnitude of the pairing energy and the energy gap of successive M.O.'s.

Each cyclopentadienyl ion has five carbons each of which has a p_z orbital perpendicular to the plane of the $C_5H_5^-$ ring. These five p_z orbitals combine to give five M.O.'s of the symmetry type: a_1 (singlet), e_1 (doublet) and e_2 (doublet). When we take into consideration the two rings alongwith their relative orientation in ferrocene the ligand symmetry orbitals may be classified into even (g) and (u) pairs: a_{1g}, a_{2u}, e_{1g}, e_{1u}, e_{2g} and e_{2u}. For ferrous iron the participating orbitals are: a_{1g} (d_{z2}; s), a_{2u} (p_z), e_{1u} (p_x, p_y) e_{1g} (d_{xz}, d_{yz}), e_{2g} (d_{xy}, $d_{x^2-y^2}$) The a_{1g} cyclopentadienyl M.O. in ferrocene has a + sign for the lower lobes of all the five carbon p_z orbitals of the upper Cp^- and + sign for the upper lobes of the p_z orbitals of the five carbon atoms of the lower Cp^-. The symmetry of this M.O. will match the metal ion $4s$ and $3d_{z^2}$ orbitals. This Cp^- M.O. contains electron pairs. Overlap of such Cp^- electron pair with the metal orbital gives $C_p \rightarrow M$ sigma bond. If we maintain the sign of the upper Cp^- the same but reverse that of the lower Cp^- we will have the a_{2u} M.O. whose symmetry will match the symmetry of the metal p_z orbital. One e_{1g} bonding M.O. has + sign in the lower lobes of two carbons (of the upper C_p^-) on one side of the nodal plane while the two other carbon atoms on the other side have a negative sign. The nodal plane passes through the fifth carbon indicating this carbon does not take part in the formation of the e_{1g} bonding M.O. If the signs are reversed for the upper lobes of the p_z orbitals of the lower Cp^- we have a gerade (g) symmetry. The other e_{1g} bonding M.O. is similar to the above e_{1g} bonding M.O. with the difference that it is at 90° to this above one. Both these e_{1g} have electron pairs. These two M.O.'s donate their electron pairs to the metal atom via overlap with its empty d_{xz} and d_{yz} orbitals to form $C_p \rightarrow M\pi$ bonds. The two degenerate e_{1u} M.O.'s have the right sign to match those of the ungerade metal orbitals p_x and p_y. There pre two degenerate e_{2u} antibonding orbitals. Each of these orbitals has two perpendicular nodes but none contains any electron pair. These M.O.'s overlap with the filled d_{xy} and $d_{x^2-y^2}$ orbitals. [For iron (II) the electron distribution is taken as $3d^2{}_{z^2}$, $3d^2{}_{xy}$, $3d^2{}_{x^2-y^2}$, $3d^0{}_{xz}$, $3d^0{}_{yz}$ i.e. $a^2{}_{1g}$, $e^4{}_{2g}$, $e^0{}_{2g}$). If we take the plane of the paper as the plane of the $d_{xy}/d_{x^2-y^2}$ orbitals then the signs of the lower lobes of the upper C_p^- in the four segments of parallel C_p^- with +, −, + and − signs will match the symmetry and signs of the d_{xy} and $d_{x^2-y^2}$ metal ion orbitals. The upper lobes of the p_z orbitals of the lower C_p^- will have matching signs. A back bonding from filled metal ion orbital to empty antibonding orbital will thus result. Since these C_p^- rings have two nodal planes it will lead to a lateral overlap giving a δ-type bond (Fig. 23.8). All the symmetry permitted metal ion orbitals and the two C_p- ring orbitals will give a set of M.O.'s which are shown in Fig. 23.9.

It is believed that in the above M.O. scheme the empty metal ion orbitals and the filled C_p^- orbitals interact to such an extent that it leads to an effective bonding but not to the extent of drawing the π-electrons solely to the metal ion—in which case the π-electrons will have more of metal character. In such a case the π-electrons will undergo addition reactions rather than substitution reactions i.e. aromaticity will be lost.

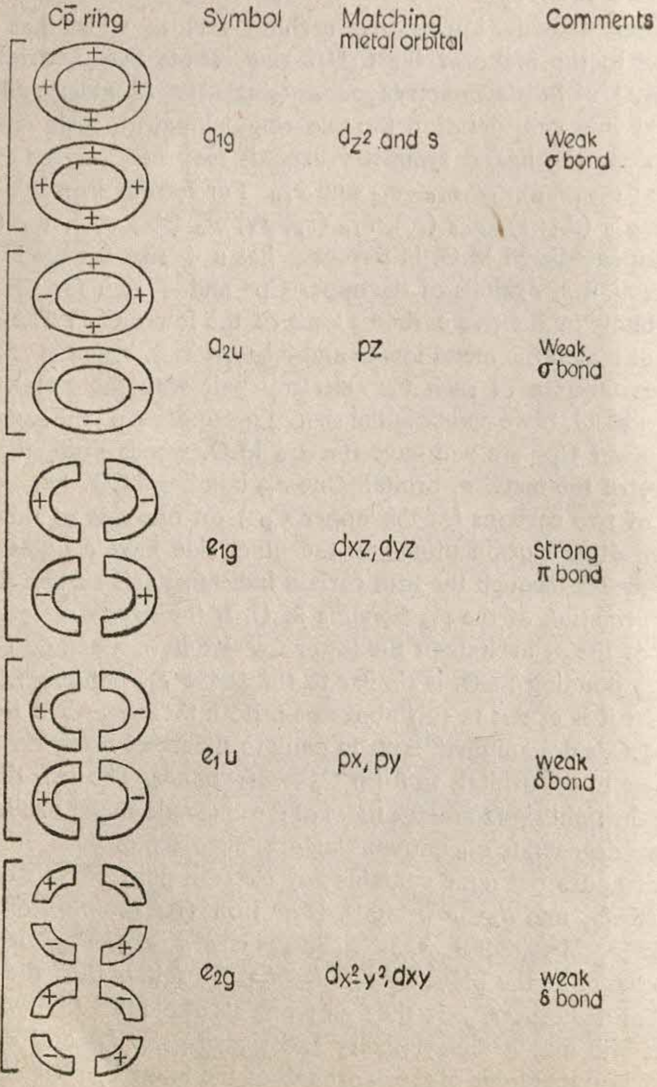


FIG. 23.8. Pictorial representations of the Cp^- ring and the matching metal orbitals.

Depending on the preferred rotational orientation of the cyclopentadienyl rings metallocene complexes may exist in either (*a*) staggered or (*b*) eclipsed conformation. Ferrocene has staggered orientation while ruthenocene has eclipsed orientation. Discussion on the bonding is not much influenced by these conformations.

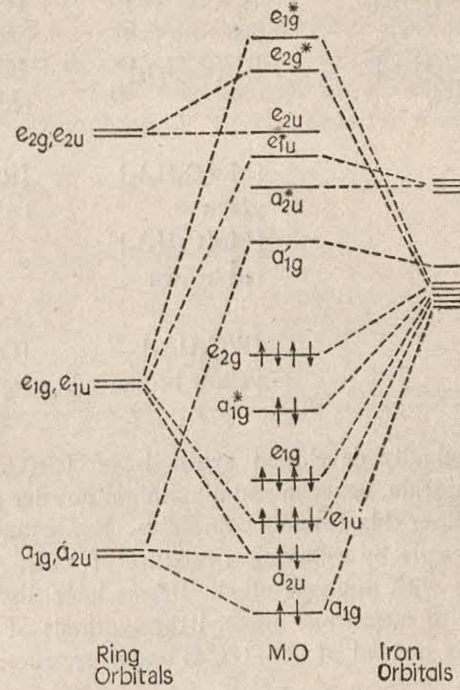


FIG. 23.9. M.O. diagram of ferrocene (after Schustorovich and Dyatkina)

23.9.3 Metal Arenes: Since the six π-electrons of $C_5H_5^-$ anion were responsible for bonding in the metallocenes it occurred to Fischer that this sort of complexation should be no monopoly of cyclopentadiene anion. Since the celebrated aromatic benzene also possesssd six π-electrons he decided to give it a real try as an organometallic ligand. The noble gas rule also gave Fischer an important clue that if $[(C_6H_6)_2M]^\circ$ complexes were to be made it was best to try with chromium because the 24 electrons of Cr° plus the 12π-electrons will take the electronic configuration of the metal to that of krypton.

Anhydrous $CrCl_3$, anhydrous $AlCl_3$, Al powder and benzene were reacted in an autoclave at 180°C when the following reaction took place:

$$3CrCl_3+2Al+AlCl_3+6C_6H_6 \rightarrow 3[Cr(C_6H_6)_2]AlCl_4$$

It was reduced by sodium dithionite to brown black bis (benzene) chromium (O) which was purified by sublimation:

$$2[Cr(C_6H_6)_2]^+ + S_2O_4^{2-} + 4OH^- \rightarrow 2[Cr(C_6H_6)_2] + 2SO_3^{2-} + 2H_2O$$

Some bis (benzene) metal complexes are listed in Table 23.5.

Table 23.5. Some bis (benzene) Metal Complexes

Group	V	VI	VIII
First Transition Series	$[V(C_6H_6)_2]$ red-brown $[V(C_6H_6)_2]^+$ yellow	$[Cr(C_6H_6)_2]$ brown-black $[Cr(C_6H_6)_2]^+$	$[Fe(mesitylene)_2]^{2+}$ orange red $[Co(mesitylene)_2]^{3+}$ red brown
Second Transition Series		$[Mo(C_6H_6)_2]$ green $[Mo(C_6H_6)_2]^+$ red brown	$[Ru(mesitylene)_2]^{2+}$ light yellow
Third Transition Series		$[WC_6H_6)_2]$ yellow brown	$[Os(mesitylene)_2]^{2+}$ light yellow

Syntheses: The originally developed synthesis of $[Cr(C_6H_6)_2]$ from metal chloride, aluminium chloride, benzene and aluminium powder proved to be highly successful for many other bis (arene) complexes. For example, bis (benzene) vanadium (O) is best made by refluxing a mixture of VCl_4, $AlCl_3$, Al and C_6H_6 followed by hydrolysis with aqueous alkali. It was later discovered by Fischer that catalytic amounts of mesitylene allowed the synthesis of $[Cr(C_6H_6)_2]$ to be carried out under reflux instead of at ~180°C under pressure.

Properties: *Bis (benzene) vanadium* (O) forms red brown crystals which are air-sensitive. It melts at 277–278°C and is soluble in organic solvents. It is one electron short of krypton configuration and thus shows paramagnetism ($\mu \sim 1.73$ B.M.).

Bis (benzene) chromium (O) forms brown black, air-sensitive crystals (M.P. 284–285°C). The compound is moderately soluble in organic solvents. This can be oxidised by air or iodine in a two-phase water/organic solvent system and the iodide, perchlorate, etc. salts of $[Cr(C_6H_6)_2]^+$ can be precipitated. Under vigorous conditions complete substitution of both C_6H_6 ligands can be effected:

$$[Cr(C_6H_6)_2] + 6PF_3 \rightarrow [Cr(PF_3)_6] + 2C_6H_6$$

Bis (benzene) molybdenum (O) forms glistening green crystals which sublime at ~90–100°C. This is soluble in organic solvents. It ignites in air.

Attempted Organic Reactions: Friedel-Crafts acylation, metallation with butyllithium, mercuration, nitration, etc. were attempted on bis (benzene) chromium (O). However no positive results were obtained. These failures have been interpreted not to mean that bis (benzene) chromium (O) is devoid of aromatic character but that the substituted products are not stable enough to survive the reaction conditions.

Structure and Bonding: Fischer and his students held the view that all the twelve π-electrons of the two benzene rings were drained into the d^2sp^3 hybrid orbitals of the metal. But this view is naive and is unacceptable now. The M.O. picture (Fig 23.10) is now the accepted view of the bonding in metal arenes. Compared to metallocenes two differences will arise: (1) there will be some alteration in the relative energies of the rings and the metal orbitals and (2) there will be two more π-M.O.'s which, however, are vacant and of much higher energy.

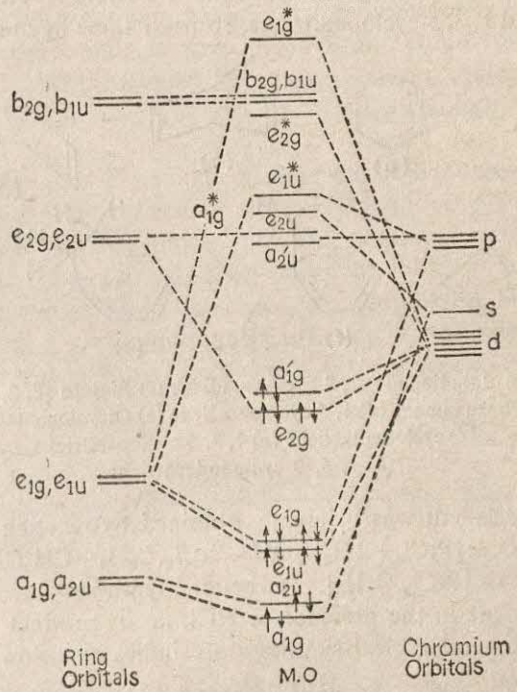
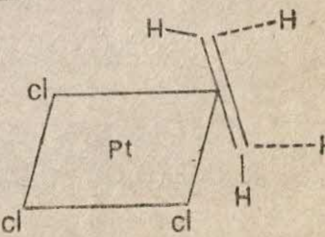


FIG. 23.10. M.O. diagram of bis(benzene) chromium (0) (after Schustorovich and Dyatkina)

23.10. METAL OLEFINS AND METAL ALKYNES

23.10.1. The Beginning: The first metal-olefin complex—indeed the first organo-metallic complex—namely $K[PtCl_3.(C_2H_4)]$ obtained by Zeise, a Danish pharmacist, in 1827 went unnoticed for over a century. It is curious to note that C_2H_4 does not possess any lone pair of electrons in the usual sense and therefore on



(23–IX)

the basis of prevailing ideas on Werner complexes one would not consider it a potential ligand. Structural studies of K $[PtCl_3(C_2H_4)]$ have shown that the square plane of platinum (II) is perpendicular to the C = C double bond and that one of the coordination points is occupied by the ethylene double bond (23–IX).

23.10.2 Metal Olefins Olefinic Ligands The mono-olefin ethylene and a variety of diolefins and triolefins have been found to form complexes with transition metals. The diolefins include both conjugated ones like butadiene and 1, 3 cyclohexadiene, and non-conjugated ones like norbornadiene, 1, 5 cyclooctadiene and dicyclopentadiene. Among the triolefins are cycloheptatriene, dimethylene bicycloheptane and 1, 3, 5-cyclooctatriene. Some of these ligands are shown below:

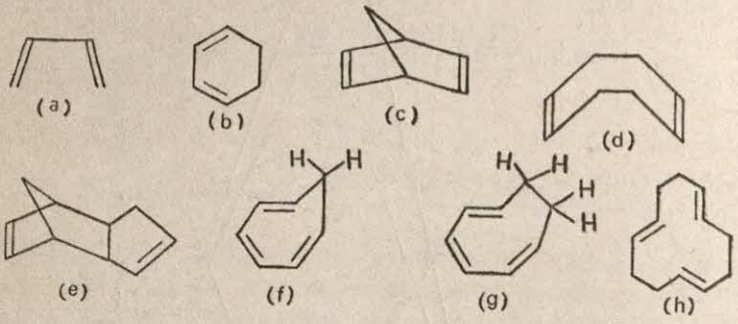


FIG. 23.11. (*a*) Butadiene (*b*) 1, 3 cyclohexadiene (*c*) Bicyclo [2, 2, 1] heptadiene (norbornadiene) (*d*) 1, 5 cyclooctadiene (*e*) Dicyclopentadiene (*f*) cycloheptatriene (*g*) 1, 3, 5 cyclooctatriene (*h*) 1, 5, 9 cyclododecatriene.

Syntheses: Zeise's salt was originally obtained by reacting Pt Cl_4 in ethanol in the presence of KCl: $[PtCl_4+2C_2H_5OH \rightarrow PtCl_2.C_2H_4+CH_3CHO+H_2O+2HCl]$ $PtCl_2.C_2H_4+KCl \rightarrow K[PtCl_3.C_2H_4]$. A better synthesis involves reaction of K_2PtCl_4 with ethylene in the presence of HCl, a by-product being the dimer $[PtCl_2(C_2H_4)]_2$. Serveral typical syntheses are indicated below:

$$K_2PtCl_4+C_2H_4 \xrightarrow{HCl} K\,[Pt(C_2H_4)Cl_3]+KCl$$

$$RhCl_3(H_2O)_3+C_2H_4 \xrightarrow[H_2O]{ROH} [(C_2H_4)_2RhCl]_2+\text{other products}$$

$$Fe_2(CO)_9+C_2H_4 \xrightarrow[50\text{ atm}]{25°C} [(C_2H_4)Fe(CO)_4]+Fe(CO)_5$$

$$(C_5H_5)Mn(CO)_3+C_2H_4 \xrightarrow{uv} [(C_5H_5)Mn(CO)_2(C_2H_4)]+CO$$

$$RhCl_3(H_2O)_3+C_8H_{12}(1,\ 5\text{ cyclooctadiene})$$

$$\xrightarrow[C_2H_5OH]{SnCl_2} [(C_8H_{12})RhCl]_2$$

Reactions: The chlorine-bridged dimer $[(C_2H_4)\,PtCl_2]_2$—a by-product during synthesis of Zeise's salt—reacts with excess ethylene at −70°C in acetone to give yellow mononuclear $[(C_2H_4)_2PtCl_2]$ which changes to the dimer mono (olefin) complex around 0°C. Corresponding palladium (II) complexes are less stable and unlike their platinum analogues are hydrolysed by water to give aldehydes and palladium metal:

$$[(C_2H_4)PdCl_2]_2 + 2H_2O \rightarrow 2CH_3CHO + 2Pd + 4HCl$$

This reaction forms the basis of the commercial palladium-metal catalysed oxidation of olefins to aldehydes.

The chlorine bridges in $[(C_2H_4)_2RhCl]_2$ and in [(1, 5-cyclooctadiene) $RhCl]_2$ can be destroyed with suitable ligands. In the presence of a base acetylacetone reacts with such compounds to give mixed ligand complexes like $[(C_2H_4)_2Rh$ (acac)] and [(1, 5 cyclooctadiene) Rh(acac)]. Sodium cyclopentadienide gives correspondingly $[(C_5H_5)Rh(C_2H_4)_2]$ and [(1, 5 cyclooctadiene) $Rh(C_5H_5)]$.

Bonding: The nature of bonding in ethylene has been discussed earlier (page 97, Part I). There is a π-bond formed by the overlap of two *p* orbitals containing one electron each. If we extend the interaction of these *p* orbitals to the M.O. model then this C—C π-interaction generates two M.O.'s—one bonding M.O. being occupied by two electrons and the other antibonding M.O. being empty. An empty σ-type metal orbital [for square planar platinum (II) it is $5d_{x^2-y^2}6s6p^2$ hybrid orbital] can now overlap the filled π-M.O. of ethylene. This ligand-to-metal

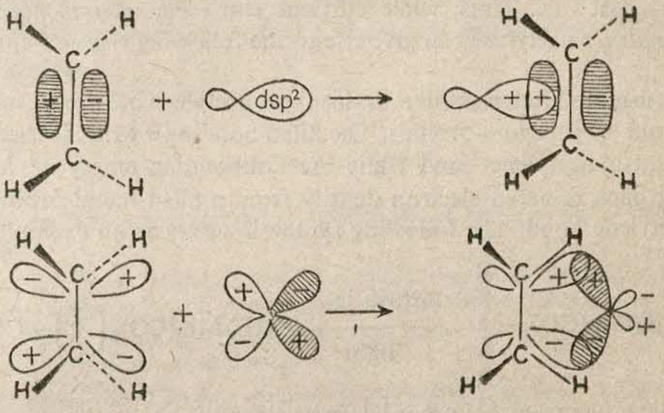
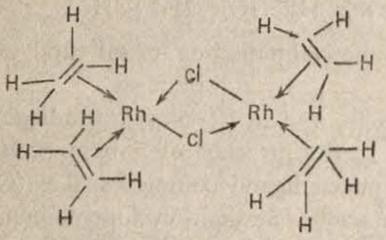


FIG. 23.12. Metal ethylene Bond

bond is not exactly like usual σ-bonds. In usual σ-bonds the electron density due to overlap of orbitals is concentrated along the internuclear bond axis. Note that the metal-olefin bond is not really concentrated along platinum—carbon bond axis but along the line joining platinum and the centre of the C—C bond. Such overlap has been named a μ bond. A filled metal π-type *d*-orbital ($5d_{xz}$ for Pt (II)) overlaps the empty antibonding π-M.O. of ethylene (Fig. 23.12). There arises, therefore, some double bond character in the bond between the metal and the olefin. That some electron drift from the double bond onto the metal has really occurred is shown by the fact that while the C—C distance in olefin is ~1.34A that in metal olefins is around ~1.40—1.45A.

A coordinated C = C bond is equivalent to one coordinate link from the ligand to the metal. Thus monoolefin functions as a monodentate ligand (23—X) while a diolefin is potentially bidentate (23—XI).



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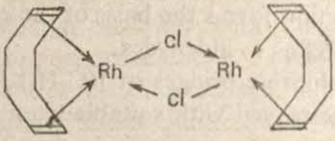
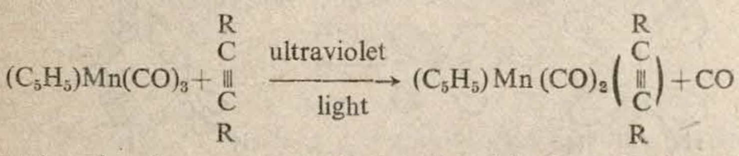


(23-XI)

23.10.3 Metal Alkynes: Acetylene, C_2H_2, is the simplest alkyne and has a triple bond between the two carbons. The two carbons are sp_x hybridised and each forms two sigma bonds with one hydrogen and the other carbon. Each carbon then has one electron each on its p_y and p_z orbitals. The overlap of these orbitals with corresponding orbitals of the other carbon generates a π_{py} M.O. (bonding) and π_{py}^* M.O. (antibonding), and π_{pz} M.O. (bonding) and π^*_{pz} M.O. (antibonding). In other words, acetylene has two π-orbitals perpendicular to each other while ethylene has just one. Thus, while ethylene can form only *monodentate monometallic complexes* acetylene can give rise to the following types of complexes:

1. **Monodentate Monometallic:** In this type, acetylene behaves just like ethylene using only one of its two π-orbitals. The filled bonding π M.O. is used in forming the sigma metal-acetylene bond while the antibonding empty π^* M.O. is used in receiving back donated electron density from a filled metal orbital forming a π-metal acetylene bond. The following synthesis serves as an example:



$$(C_5H_5)Mn(CO)_3 + \begin{matrix} R \\ C \\ ||| \\ C \\ R \end{matrix} \xrightarrow[\text{light}]{\text{ultraviolet}} (C_5H_5)Mn(CO)_2\left(\begin{matrix} R \\ C \\ ||| \\ C \\ R \end{matrix}\right) + CO$$

That acetylene functions as a monodentate ligand is shown by its replacing only one CO group.

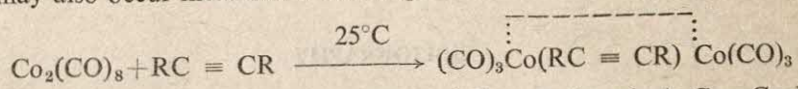
2. **Bidentate Monometallic:** Here the ligand utilises both the π-orbitals for coordination to the metal. Two sigma orbitals and two π-orbitals of the metal are involved while two π-orbitals and two π^*-orbitals (approximately at 90°) of acetylene are involved in the bonding.

$$(C_5H_5)V(CO)_4 + RC \equiv CR \xrightarrow[\text{light}]{\text{ultraviolet}} (C_5H_5)V(CO)_2(RC \equiv CR) + 2CO$$

$$(CH_3CN)_3W(CO)_3+3RC \equiv CR \xrightarrow{80°C} (RC \equiv CR)_3W(CO)+3CH_3CN+2CO$$

Note that one acetylene group displaces two CO groups from the vanadium carbonyl.

3. **Bidentate Bimetallic:** In this case two metal atoms face the two bonding π—M.O.'s of acetylene to make the metal-ligand (C—C) axis—metal angle ~ 90°. There may also occur metal-metal bonding.



$$Co_2(CO)_8+RC \equiv CR \xrightarrow{25°C} (CO)_3Co(RC \equiv CR)\,Co(CO)_3$$

Acetylene is functioning now as a bridging bidentate ligand. A Co—Co bond helps cobalt to attain a stable noble gas configuration $(27+(3\times2)+2+1 = 36)$.

23.9. A FITTING FINALE

Alfred Werner was awarded the Nobel Prize in chemistry for 1913 for brilliantly demonstrating his coordination theory. Since that time despite many outstanding achievements such awards have eluded inorganic chemists. After sixty long years the inorganic chemistry camps all over the world went jubilant when the Nobel Prize in chemistry for 1973 was jointly awarded to Wilkinson of London and to Fischer of Munich. While the 1913 award recognised the classical Werner complexes the 1973 award was a recognition of the efforts of two great pioneers towards elucidation of the chemistry of the non-Werner organometallic complexes.

STUDY QUESTIONS

1. What are the basic requirements for stabilisation of high and low oxidation states of transition metals?

2. Discuss which of the following compounds will serve well as ligands for low oxidation state stabilisation: (*a*) ammonia, (*b*) triphenylphosphine, (*c*) triphenylphosphine oxide, (*d*) water, (*e*) ethylenediamine, (*f*) ethylenediaminetetraacetic acid, (*g*) o-phenylenebisdimethylarsine, (*h*) carbon monoxide and (*i*) carbon dioxide.

3. What is synergic effect? Explain with reference to carbon monoxide and carbonyls.

4. Give an account of metal carbonyls.

5. Nitric oxide is an odd electron molecule. Its chemistry is mostly dominated by a tendency to lose the odd electron. Discuss.

6. Discuss the bonding in metal carbonyls and show that the same bonding scheme can be extended to metal nitrosyls and metal cyanides.

7. CO forms complexes with low-valent metals but not with halides of Al and B which are strong Lewis acids. Comment.

8. Present a comparative assessment of carbon monoxide and isocyanide as a σ-donor and a π-acceptor.

9. Give an account of dinitrogen complexes including syntheses and the nature of bonding.

10. Discuss the molecular orbital picture of dioxygen and the nature of bonding in dioxygen complexes.

11. What do you understand by the term 'aromaticity'? Give some examples to show that ferrocene is aromatic in nature.

12. Discuss in details the type of bonding in ferrocene.

13. What is Zeise's salt? How is this synthesised. Give an account of the bonding in this compound.

14. "A multiple bond is a potential donor." — Discuss.

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24

Group IVA. Titanium, Zirconium and Hafnium

Titanium, zirconium and hafnium constitute group IVA of the Periodic Table. Titanium occupies ninth position in the abundance list of the elements in the earth's crust. Above titanium in abundance are oxygen (47%), silicon (27.7%), aluminium (8%), iron (5%), calcium (3.4%), sodium (2.5%), potassium (2.4%) and magnesium (2.0%). Practically all crystalline rocks, sands, soils contain some amount of titanium. Two titanium ores *ilmenite* ($FeTiO_3$) and *rutile* (TiO_2) are of commercial importance. Zirconium is not really a rare element. Its total occurrence in the earth's crust exceeds the total percentage of copper, lead and zinc. However it does not occur widely in concentrated forms. It ranks twentieth in the abundance list. Hafnium is very rare and is present in minute amounts alongwith zirconium. The relative abundances are: Ti(0.06%), Zr(0.025%) and Hf(0.0005%).

24.1. COMPARATIVE STUDY OF THE GROUP IVA ELEMENTS

24.1.1. General Considerations: This group consists of the elements titanium, zirconium and hafnium. In the past thorium used to be included in this group after hafnium but now thorium goes with the actinides. All the elements possess outside a noble gas core a d^2s^2 configuration (Table 24.1).

Table 24.1. Electronic Configuration and Some Properties of Group IVA Elements

Element	Atomic Number	Electronic Configuration	Ionisation Potential (*e.v.*)	Electronegativity
Titanium	22	$[Ar]3d^2 4s^2$	6.82, 13.57, 27.47, 43.24	1.5
Zirconium	40	$[Kr]4d^2 5s^2$	6.84, 13.13, 22.98, 34.33	1.4
Hafnium	72	$[Xe]4f^{14} 5d^2 6s^2$	. . . .	1.3

It is possible to extract or utilise the outer electrons in a stepwise fashion to get several valences. The different oxidation states observed experimentally with these elements are given below (bold ones are the stablest and the italicised ones come next in stability):

Ti	**+4**	*+3*	+2	0	−1
Zr	**+4**	*+3*	....	0	...
Hf	**+4**	*+3*	...	...	...

The lower valences become increasingly unstable with increasing atomic number. With the non-transition elements of group IVB, namely carbon, silicon, germanium, tin and lead the main valence is the group valence +4. Valence +2 occurs in group IVB due to an inert pair effect, the effect increasing with atomic number. Thus +2 state becomes the common and dominating valence with tin and lead.

Some general features in the chemistry of group IVA follow from the size and charge of the ions. We had earlier (Chapter 22) seen that the size increase between the first and second members of a group is always appreciable but the difference is minimal between the third and the second. This is due to a lanthanide type contraction in Hf because of the $4f$ electrons. Thus M^{4+} radius for Ti, Zr and Hf are 0.68A, 0.80A and 0.81A respectively (Table 24.2). Because of the very close atomic and ionic radii the chemistries of Zr and Hf are very similar. Their ionic potentials are the same. Overall ionisation potentials for four electron loss expectedly decrease from Ti to Zr in keeping with an increase in size. There is a small decrease in electronegativity. Expectedly the standard potentials of the MO^{2+}/M couples become more negative from Ti to Hf. A two-fold increase in the density of Hf compared to that of Zr is due to a two-fold increase in atomic weight from Zr(91) to Hf(179) although the size remains the same (Table 24.2).

Table 24.2. Some More Properties of Group IVA Elements

Element	Atomic Radius(A)	Ionic (M^{4+}) Radius(A)	M.P. (°C)	B.P. (°C)	Density (gm/ml)	$E°$, (volts) $MO^{2+}+2e \rightleftharpoons M$
Titanium	1.47	0.68	1725	3260	4.50	−0.95
Zirconium	1.60	0.80	1860	3580	6.53	−1.53
Hafnium	1.59	0.81	2200	5400	13.07	−1.68

Fajans' generalisations are valid on many points. For example the higher oxidation states give mostly covalent compounds. The lower valences are more ionic and reducing. TiO^{2+}/Ti^{3+} couple has an $E°$ value +0.10 volts so that Ti^{3+} will easily reduce Fe^{3+} to Fe^{2+} ($E° = 0.77$ volts), chlorates and perchlorates to chlorides. The still lower valences become more unstable and more difficult to obtain. The 0 and −1 oxidation states can be had only with π-bonding ligands such as dipyridyl. That lower valences become increasingly less stable with increasing atomic number is shown by the instability of ZrI_3 and $ZrBr_3$.

Following Fajans' rules we find titanium to be the most complexing in the group. Availability of *d*-orbitals with Ti, Zr and Hf makes nucleophilic attack on the tetrahalides possible leading to their hydrolysis. In keeping with the general properties of transition metals their compounds become coloured when the ions have incomplete *d*-level. Thus $3d^1$ Ti^{3+} aquo complex $[Ti(H_2O)_6]^{3+}$ shows a $d-d$ transition (from t_{2g} to e_g) that makes the complex look violet (Chapter 10). The single electron also makes the compound paramagnetic ($\mu \sim 1.7$ B.M.). The quadrivalent $3d^0$ compounds are, of course, all diamagnetic.

24.1.2. Chemical Behaviour. *Hydrides:* We have already seen that the transition metal hydrides do not conform to any definite stoichiometry. Indeed the tiny hydrogen moves into the interstices of the metal structure. The formula of the hydrides are: $TiH_{1.75}$, $ZrH_{1.92}$.

Oxides and Hydroxides: No definite hydroxides $M(OH)_4$ are known. The 'hydroxides' are really hydrated oxides. The acidity of the hydrated oxides falls in the order $Ti > Zr > Hf$. Titanium oxide is amphoteric. It can form alkali titanate, eg: K_2TiO_3, which is readily hydrolysed by water. Zirconium oxide is less acidic and more basic. Accordingly it is practically insoluble in excess alkali. Hafnium oxide behaves similarly.

Halides: The tetrahalides (MX_4; X = Cl, Br, I) of Ti, Zr and Hf are covalent compounds as is evident from their comparatively low melting points and boiling points, by their non-electrolytic nature and solubility in organic solvents. In the vapour state these are monomeric and tetrahedral. TiF_4 and $TiCl_4$ are colourless, $TiBr_4$ is yellow and TiI_4 is red-brown. The tetrahalides are readily hydrolysed.

Element	MF_4	MCl_4	MBr_4	MI_4
Ti	284	−23°(136)	38(230)	150(377) M.P.°C (B.P.°C)
Zr	....	331 (subl.)	357	431
Hf	....	319 (subl.)	420 (subl.)	...

The extent of hydrolysis by water, however, decreases from Ti to Zr. TiX_4 compounds are hydrolysed to TiO_2 whereas ZrX_4 and HfX_4 give $ZrOX_2$ and $HfOX_2$ in water. ZrO_2 and HfO_2 are obtained only on the addition of alkali.

Salts of Oxyacids: Due to their weak basic properties, these elements hardly give any normal salt of oxyacids. All salts crystallised from water are of the oxy-type: $TiOSO_4$, $ZrOCl_2$, $ZrO(NO_3)_2$, etc.

Complexes: Titanium tetrachloride and tetrabromide are known to act as good Lewis acids. Thus adducts with triphenylphosphine $TiCl_4.2PPh_3$, alcohols etc. are known. The commonest coordination number is six, although 4, 7 and 8 have also been claimed. Oxygen donor chelates with catechol, acetylacetone, oxalic acid are also known. With coordination number 4 the compounds are tetrahedral, with 6 compounds are octahedral. Some common examples of complexes are $TiCl_4.2PPh_3$, $[TiF_6]^{2-}$, $TiCl_2$ (acac)$_2$ etc. The tendency to assume higher coordination number increases with Zr and Hf due to increased size. Examples are $Na_3[ZrF_7]$, $Na_3[HfF_7]$. *o*-Phenylenebisdimethylarsine (diars) forms a complex $ZrCl_4$.2 diars which has an eight-coordinate structure.

24.2. OXIDATION STATES OF TITANIUM

24.2.1. Quadrivalent Titanium. *Titanium Dioxide:* This is of enormous commercial importance for its use as a white pigment. This is generally obtained by two methods. In one procedure *ilmenite* ($FeTiO_3$) is digested with H_2SO_4 whereby $FeSO_4$ and $TiOSO_4$ are produced. Some ferric sulphate contaminant is reduced to $FeSO_4$ by heating with scrap iron. The final solution is concentrated when *green vitriol* ($FeSO_4.7H_2O$) crystallises. The filtrate is hydrolysed to get TiO_2. Alternatively $TiCl_4$ is made to react with air in the gas phase.

Titanium (IV) Halides: $TiCl_4$ is made either by reacting titanium and chlorine, or by passing chlorine over a mixture of TiO_2 and carbon:

$$TiO_2+C+2Cl_2 \rightarrow TiCl_4+CO_2$$

It is a non-electrolytic covalent compound and has a very low dielectric constant 2.7 (H_2O, 78.5). It is a good Lewis acid and forms adducts with ethers, amines, alcohols, heterocyclic bases etc. Adducts are also known with P, As and S donors. It is readily hydrolysed by water and fumes in moist air:

$$TiCl_4+2H_2O \rightarrow TiO_2+4HCl$$

Reaction of $TiCl_4$ vapour with KCl, RbCl, etc. give hexachloro complexes $M_2^I[TiCl_6]$.$TiCl_4$ forms alcohol adducts, ROH.$TiCl_4$ and phosphine adducts $TiCl_4.2PPh_3$.

$TiBr_4$ and TiI_4 are crystalline compounds. Their behaviour is similar to that of $TiCl_4$. The tetrafluoride also adds fluoride ions to form hexafluoro complexes.

24.2.2. Trivalent Titanium. Titanium (III) is obtained by the reduction of titanium (IV) solution at the cathode or by zinc amalgam or by zinc and acid. For cathodic reduction a diaphragmed cell is used. A porous pot fitted into a beaker through a suitable rubber bung serves the purpose. Catholyte is a solution of $TiCl_4$ in HCl or $TiOSO_4$ in H_2SO_4. Overall acidity is $4N$. The anolyte is the corresponding acid. Sheet lead is used as cathode and a graphite rod as anode. The violet solution thus obtained is extremely susceptible to air and has to be worked up in an inert atmosphere. Tervalent titanium is a strong reducing agent (TiO^{2+}/Ti^{3+}, $E^\circ = 0.10$ volts). A comparison with the couples Fe^{3+}/Fe^{2+} ($E^\circ =$ 0.77 volts) and Sn^{4+}/Sn^{2+} ($E^\circ = 0.15$ volts) shows that Sn^{2+} can reduce Fe^{3+} but not TiO^{2+}.Ti^{3+} is a stronger reducing agent than both Fe^{2+} and Sn^{2+}. It readily reduces permanganate to manganous state:

$$5Ti^{3+}+MnO_4^-+H_2O \rightarrow 5TiO^{2+}+2H^++Mn^{2+}$$

The violet titanium (III) solution gives crystals of $[Ti(H_2O)_6]Cl_3$ from HCl solution. The violet solution on saturation with HCl under ether gives a green isomer presumably related to the violet as hydration (or ionisation) isomer. Anhydrous $TiCl_3$ is obtained as a violet powder on reduction of $TiCl_4$ vapour by hydrogen around 650°C.$2TiCl_4 + H_2 \rightarrow 2TiCl_3 + 2HCl$ Ti(III) is expectedly more basic than Ti(IV). This is shown by the absence of any oxysalt. Unlike Ti(IV), titanium (III) gives a normal oxalate and a sulphate. Typical of many trivalent cations it forms alums with large monovalent cations, $CsTi(SO_4)_2.12H_2O$ being a typical example. Titanium (III) is a 3 d^1 system and hence all its compounds are expected to show a spin magnetic moment of 1.73 B. M. in magnetically dilute state.

Complexes of trivalent titanium have not been extensively studied. Some well established complexes are: $[Ti(acac)_3]$, $[TiF_6]^{3-}$, $[TiCl_5(H_2O)]^{2-}$ etc. All such complexes are easily oxidised to oxotitanium (IV) complexes such as $[TiO(acac)_2]$. The power of complex formation decreases from +4 to +3 state because of smaller charge and larger size.

Electronic Spectra: Titanium (III) is a $3d^1$ system and therefore it has only one spin allowed but Laporte forbidden transition, namely $^2T_{2g} \rightarrow {}^2E_g$ ($t^1_{2g} \rightarrow e^1_g$) (Chapter 11, page 274). The violet colour of $[Ti(H_2O)_6]^{3+}$ (Fig. 24.1) has an absorption band at 20,300 cm^{-1} (20.3 kK; 493 nm) corresponding to this transtion (= 10 *Dq*). The rather broad, asymmetric nature of the absorption band is ascribed to Jahn Teller effect. Recall that here both the ground state (*T* term) and the excited state (*E*) are Jahn Teller sensitive (Chapter 10, page 237). A complex with a stronger ligand eg: $[Ti(CN)_6)]^{3-}$ will absorb at a still higher energy (22.3 kK). The following absorption energies may be noted:

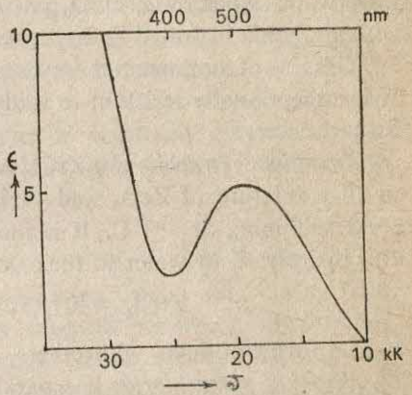

FIG. 24.1. Electromic spectium of $[Ti(H_2O)_6]^{3+}$

$[TiBr_6]^{3-}$	... 10.5 kK	$[Ti(H_2O)_6]^{3+}$	... 20.3kK
$[TiCl_6]^{3-}$	... 13.0 ,,	$[Ti(dipy)_3]^{3+}$	... 21.2 ,,
$[Ti(urea)_6]^{3+}$	... 17.3 ,,	$[Ti(CN)_6]^{3-}$	... 22.3 ,,

24.2.3. Other Low Oxidation States. Bivalent titanium is very unstable. $TiCl_2$ has been obtained by the reduction of $TiCl_4$ by Ti. $TiCl_2$ cannot survive in aqueous medium since it is oxidised by water to TiO_2 or oxotitanium (IV) salt. The extremely low oxidation states are known only in the form of π-acid complexes. Herzog has successfully reduced $TiCl_4$ in presence of dipyridyl in tetrahydrofuran solvent by metallic lithium. The complexes $[Ti(dipy)_3]$ and $Li[Ti(dipy)_3]$ have been obtained as black or dark purple needles. It is worthwhile to remark that none of titanium, zirconium and hafnium forms any carbonyl complex.

24.3. OXIDATION STATES OF ZIRCONIUM AND HAFNIUM

24.3.1. Quadrivalent Zirconium and Hafnium. *Zirconium dioxide:* It may be obtained from *zircon* ($ZrSiO_4$) by NaOH fusion and leaching with water whereby sodium silicate stays in solution and impure ZrO_2 is precipitated. This is then converted by HCl to $ZrOCl_2$. Some unattacked zircon is carried with ZrO_2. The HCl treatment attacks the zircon and separates silica. The filtrate from this treatment is made basic with ammonia when hydrated ZrO_2 separates. In another procedure natural *baddeleyite* (ZrO_2) is boiled with HCl to remove soluble impurities. The unattacked ZrO_2 is then fused with bisulphate and then leached with water whereby $ZrOSO_4$ passes into solution. On hydrolysing the sulphate with ammonia hydrated ZrO_2 is precipitated.

This is of commercial importance because of its usefulness as a pigment. It is exceptionally resistant to acids and alkalies, and is therefore used in making furnace cores.

Zirconium tetrachloride: $ZrCl_4$ is obtained by chlorination of heated zirconium or of a mixture of ZrO_2 and carbon. It closely resembles $TiCl_4$. It is a white solid subliming at 331°C. It is monomeric and tetrahedral in the vapour state. It is hydrolysed by water to the oxychloride stage:

$$ZrCl_4 + 9H_2O \rightarrow ZrOCl_2.8H_2O + 2HCl$$

It also forms adducts with ethers, esters, amines, As-donors, etc.

Hafnium tetrachloride has parallel behaviour.

24.3.2. Lower Oxidation States of Zirconium and Hafnium. The lower oxidation states of these elements are difficult to make and are little known. $ZrBr_4$ and H_2 react at 450°C over Al to give $ZrBr_3$ and $ZrBr_2$. These have also been made by reduction with powdered zinc.

The reduction of the tetrahalides by respective metals within the temperature range 200—700°C and pressure range 5—15 atmosphere have also been carried out to get the compounds $ZrCl_3$, $ZrBr_3$, ZrI_3, $HfCl_3$, $HfBr_3$ and HfI_3;

$$3MX_4 + M \rightleftharpoons 4MX_3$$

These trihalides are coloured brown to reddish brown.

A zerovalent zirconium complex $[Zr(dipy)_3]$ has been obtained by reduction of $ZrCl_4$ by lithium in the presence of dipyridyl in tetrahydrofuran.

24.4. ISOLATION OF THE GROUP IVA ELEMENTS

24.4.1. Titanium. The best known ores are *ilmenite* ($FeTiO_3$) and *rutile* (TiO_2). Common carbon reduction is not feasible since the metal forms a stable carbide. At elevated temperature oxide formation also occurs. It is generally made by the following Kroll process. Chlorine is passed over an intimate mixture of *ilmenite* or *rutile* and carbon at 900°C:

$$2TiO_2 + 3C + 4Cl_2 \rightarrow 2TiCl_4 + 2CO + CO_2$$

$$2FeTiO_3 + 6C + 7Cl_2 \rightarrow 2FeCl_3 + 2TiCl_4 + 6CO$$

The $TiCl_4$ is condensed and purified from $FeCl_3$ by fractional distillation (B.P.°C, $TiCl_4$, 136; $FeCl_3$, 315). $TiCl_4$ vapour is next made to react with molten magnesium at 800°C in argon atmosphere:

$$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$$

The titanium is then freed from magnesium and magnesium chloride by volatilising these at 1000°C in argon atmosphere. Finally the titanium is fused in argon atmosphere and cast into rods. Very pure titanium is obtained by the following van Arkel—de Boer process. The crude powdered titanium alongwith a little iodine is taken in a glass vessel into the centre of which is sealed a thin tungsten filament. The vessel is evacuated and the filament electrically heated to 1300°C. The glass vessel with the titanium powder is heated to 150°C. Under these conditions the iodine reacts with Ti to form TiI_4 which is thermally dissociated into pure titanium on the tungsten filament. The iodine again combines with crude titanium and the process becomes self sustaining.

24.4.2. Zirconium and Hafnium. Best known ores of zirconium are *zircon*, $ZrSiO_4$, and *baddeleyite*, ZrO_2. Beach sands containing zircon are concentrated by gravity methods and final cleaning done by magnetic separator. Zircon concentrates are then mixed with carbon and heated in an arc furnace whereby zirconium carbide (ZrC) is formed. Sometimes nitrogen is also introduced during the heating whereby a mixed zirconium carbide-nitride is formed. This product readily reacts with chlorine giving a good quality zirconium tetrachloride. $SiCl_4$ (B.P. 57°C) can he easily got rid of.

Alternatively zircon can be fused with NaOH and leached with boiling water. Most of the silicate passes into solution as sodium silicate leaving crude ZrO_2 which is further purified as described in 24.3.1. The purified ZrO_2 is then treated with chlorine in the presence of carbon. This procedure yields pure $ZrCl_4$.

Pure zirconium is obtained from $ZrCl_4$ by following the Kroll technique.

Separation of Zirconium and Hafnium: Zircon carries about 0.5—2.0% hafnia and all extraction procedures for zirconium also lead to the extraction of hafnium. Both the elements have the same atomic radii ($\simeq$1.6A) and ionic radii (M^{4+}, 0.8A). Their charge by radius ratio is the same. Thus their chemistries are very similar so that no straightforward chemical method can be devised for their separation and independent extraction. The only hope lies in some slight difference in their extraction behaviour or in the solubility of their compounds. The many different methods devised so far are: (1) fractional crystallisation of the double fluorides, (2) elution of their tetrachlorides from a silica gel column by acids of different concentrations, (3) extraction of crude zirconyl chloride with thiocyanate-rich isobutyl ketone.

1. *Fractional Crystallisation of the Double Fluorides:* The solubilities of $(NH_4)_2[ZrF_6]$ and $(NH_4)_2[HfF_6]$ in water are as given below (in moles /litre):

$(NH_4)_2ZrF_6$	0.611	at 0°C
$(NH_4)_2HfF_6$	0.891	at 0°C

It is thus possible to achieve a reasonable separation by repeated crystallisation from water.

2. *Elution of the Tetrachlorides from a Silica gel Column:* Anhydrous methanol solution of the tetrachlorides is passed through a silica gel column. The fixed chlorides are then eluted first with $\sim 2N$ HCl in methanol which removes zirconium chloride. Finally elution is carried out with $7N$ H_2SO_4 which removes hafnium.

3. *Extraction of the -yl Chlorides with Thiocyanate-rich Methyl Isobutyl Ketone (MIBK):* Crude $ZrOCl_2$ is treated with a counter current stream of thiocyanate-rich MIBK. Hafnyl chloride moves into the ketone layer. Hafnium is preferentially extracted being contaminated with less than 2% zirconium. MIBK extract is then stripped with aqueous HCl, and then with aqueous H_2SO_4 whereby hafnium is brought into the aqueous layer. It is then precipitated with NH_4OH and ignited to oxide. The unextracted zirconium is recovered as ZrO_2.

24.5. USES OF THE GROUP IVA ELEMENTS

Titanium: Because of the high strength and low density of titanium alloys it finds extensive use in the construction of aircrafts and missiles. Titanium is used as crack stopper in aeroplane parts since cracks do not propagate through titanium as readily as through other metals. Due to its corrosion resistance properties it also finds use in the making of pumps, heat exchange tubes and valves. Titanium has also excellent resistance to corrosive sea water. It is therefore used for propeller shafts, anchors and other parts which are frequently exposed to sea water.

Zirconium: It has a low absorption cross section for neutrons. Hence its chief use is in the making of the core of a nuclear reactor. Other uses of the metal lie in its resistance to corrosion particularly to both acids and alkalies. Like titanium it is also used in pumps, valves, heat exchangers, pipings etc.

Hafnium : It has adequate absorption cross section for thermal neutrons and hence is used as control rod in nuclear reactors. It is sometimes used as a filament in incandescent lamps and also as cathode in X-ray tube. It is also used in rectifiers.

24.6. ANALYTICAL REACTIONS OF THE GROUP IVA ELEMENTS

Titanium: Titanium is precipitated as $TiO_2.nH_2O$ alongwith $Fe(OH)_3$ in group IIIA of the qualitative scheme. The precipitate is dissolved in dilute acid and the ferric colour is discharged by the addition of H_3PO_4. The solution is then treated with H_2O_2 when an orange-yellow colour develops. The colour is due to the formation of peroxy titanic oxide $TiO(-O_2-).nH_2O$ or to the disulphato peroxytitanic acid $H_2[Ti(-O_2-)(SO_4)_2]$. Fluoride ion discharges this colour due to the formation of colourless hexafluoro complex $[TiF_6]^{2-}$.

For quantitative estimation titanium (IV) can be precipitated by cupferron (ammonium salt of N-nitroso-N-phenyl hydroxylamine) from 5–10% H_2SO_4 medium. The yellow precipitate is rapidly filtered and ignited to TiO_2. The metal ion can be precipitated from ~ 0.025*N* HCl solution by 5, 7 dibromo-8-hydroxyquinoline (5, 7-oxin H) as [TiO(5, 7-oxin)$_2$]. It is dried at 120°C and weighed.

Zirconium: This also appears in group IIIA of the qualitative scheme. On the addition of H_2O_2 a white precipitate of zirconium peroxide $ZrO_3.nH_2O$ appears. Zirconium also forms a very characteristic phosphate $Zr(HPO_4)_2$ even from solution which is 10% in H_2SO_4. For quantitative determination the phosphate precipitate is collected and ignited to ZrP_2O_7.

STUDY QUESTIONS

1. Give a comparative account of the elements titanium, zirconium and hafnium.

2. In what respects the chemistries of group IVA and IVB are expected to vary?

3. What makes the chemistries of zirconium and hafnium so very similar? Do you think that such closely related pairs will be found in other Periodic groups?

4. Describe the techniques by which zirconium and hafnium have been separated from each other.

5. Write short accounts of trivalent titanium and trivalent zirconium and hafnium.

6. Discuss how the chemistry of titanium is expected to vary as we move from the oxidation state +4 to −1.

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25

Group VA. Vanadium, Niobium and Tantalum

Vanadium is one of the more abundant trace elements. It is widely spread in minute quantities but is found in a few concentrated forms only, as in *vanadinite*, $Pb_5(VO_4)_3Cl$, *carnotite*, $2K(UO_2)(VO_4)3H_2O$. Niobium (older name columbium, Cb) and tantalum, like the pair zirconium and hafnium, go together and are really rare. Niobium is almost eleven times as abundant as tantalum. They occur in concentrated forms in *ferrous niobate*, $Fe(NbO_3)_2$ and *ferrous tantalate* $Fe(TaO_3)_2$. The relative abundances of the three elements are V(0.02%); Nb(0.0024%); Ta(0.00021%).

25.1. COMPARATIVE STUDY OF THE GROUP VA ELEMENTS

25.1.1. General Considerations. This group consists of the transition elements vanadium, niobium and tantalum. They all possess the outer orbital configuration d^3s^2 (Table 25.1).

Table 25.1. Electronic Configuration and Some Properties of Group VA Elements

Elements	Atomic* Number	Electronic Configuration	Ionisation Potential (*ev*)	Electro-negativity
Vanadium	23	[Ar] $3d^34s^2$	6.74, 14.65, 29.31, 48, 65.2,	1.6
Niobium	41	[Kr] $4d^35s^2$	6.88, 14.32, 25.04, 38.3, 50,	1.6
Tanatalum	73	[Xe] $4f^{14}5d^36s^2$	7.88, 16.2	1.5

General features of transition elements are observed in this group also. On the whole the differences between the first two members are rather wide but the differences between the second and the third are minimal. Indeed niobium and tantalum form a very close pair. All the three elements exhibit several valences:

Vanadium	**+5**	*+4*	+3	+2	+1	0	−1
Niobium	**+5**	+4	....	....	+1	0	−1
Tantalum	**+5**	+4	....	....	+1	...	−1

The highest oxidation state is acidic and the lower ones become progressively more basic. The lower oxidation states are natutally reducing in character. The lower valences, however, become less stable with increasing atomic number. The extremely low oxidation states are stabilised, as expected (Chapter 23) by π-acid ligands such as carbon monoxide, dipyridyl, etc.

It may be recalled that in group VB elements a +3 oxidation state was exhibited outside the group valence +5. It should be remembered that the +3 state in these elements is caused by the inertness of the s^2 electron pair of the s^2p^3 outer orbital configuration.

The overall ionisation potentials for withdrawal of all five electrons are much too high to be compensated by lattice energies. Therefore following Fajans' generalisations, all pentavalent compounds are covalent. With decrease in valence the element becomes more basic, and ionic behaviour predominates. In extremely low oxidation state covalence predominates due to double bonding effect between the metal and the π-acid ligand (say, CO).

Atomic radii and ionic radii (Table 25.2) increase from vanadium to niobium but thereafter it is steady in tantalum. In tantalum we have the 4*f* electrons and hence a lanthanide type contraction takes place. This steady size but a huge increase in atomic weight from 93 (niobium) to 181 (tantalum) leads to a two-fold increase in density. The very close atomic and ionic radii of niobium (V) and tantalum (V) lead to very similar properties. The standard potentials are negative which indicates some reducing ability of the metals but the elements easily become passive in presence of acids.

Table 25.2. Some More Properties of Group VA Elements

Element	Atomic Radius(A)	Ionic (M^{5+}) Radius (A)	M.P. (°C)	B.P. (°C)	Density (gm/ml)	$E°$, volts $M^{5+} + 5e \rightleftharpoons M$
Vanadium	1.36	0.56	1919	3000	6.1	—
Niobium	1.46	0.70	2468	4927	8.4	−0.6
Tantalum	1.46	0.73	2996	6100	16.6	−0.7

Characteristic of transition elements, many of the compounds of these elements are coloured. Thus vanadium is colourless in +5 state ($3d^0$), blue or green in +4 state ($3d^1$), green in +3 state ($3d^2$) and violet in +2 state ($3d^3$) etc. Furthermore magnetic properties of their compounds are indicative of zero, one, two and three unpaired spins in the oxidation states +5, +4, +3 and +2 respectively. Once again it should be remembered (Chapter 22) that spin pairing will be favoured in niobium and tantalum than in vanadium. For example VCl_4 is paramagnetic but $NbCl_4$ is diamagnetic through polymerisation and spin—spin interaction.

25.1.2. Chemical Behaviour. *Hydrides:* The hydrides are all of interstitial type and are non-stoichiometric. They approximate to the formula, $VH_{9\cdot71}$, $NbH_{0\cdot86}$, $TaH_{0\cdot76}$.

Oxides and Hydroxides: The highest oxide of vanadium, V_2O_5, (obtained by burning vanadium in air or by adding acids to a solution of vanadate) is a yellow powder. This dissolves readily in alkalies to form vanadates. An aqueous solution of a vanadate may be really complicated depending on the pH of the solution. The oxide also dissolves in acids to give again a series of complicated formula (section **25.2.1**) depending on pH. The quadrivalent oxide VO_2 (obtained by the reduction of V_2O_5 with oxalic acid) is amphoteric. It dissolves in acids to form vanadyl salts $VOSO_4$, $VOCl_2$, etc. and in strong alkalies to form vanadates (IV) such as $M_2{}^1V_4O_9$, $M^{11}VO_3$, etc. The trivalent oxide V_2O_3 (obtained by the reduction of V_2O_5 by H_2) is a purely basic oxide. This dissolves in acids to give trivalent V^{3+} ion, which gives characteristic *alums*. On further reduction of V_2O_3 by vanadium we get VO which is also a basic oxide. The basic character is exhibited by its forming *vitriol* and double sulphates of the schönite type.

Niobic acid and tantalic acid are hydrated pentoxides. These are precipitated from alkali niobates and tantalates by acids. These are weak acidic oxides as is revealed by their precipitation from alkali niobates and tantalates by CO_2. The only acid in which these oxides dissolve is HF, and that too, is due to the formation of fluorocomplexes $[NbOF_5]^{2-}$ and $[TaF_7]^{2-}$. Reduction of the pentoxides by magnesium or hydrogen give NbO_2 and TaO_2, which are insoluble in water and acids. These are oxidised in hot alkalies to niobates and tantalates.

Halides: A wide variety of halides are known (Table 25.3). In the +5 state only VF_5 is known for vanadium but for Nb and Ta pentafluorides, pentachlorides and pentabromides are known. As demanded by Fajans' rules all the pentahalides are covalent. They fume in air, dissolve in non-aqueous solvents and register poor conductance. They are hydrolysed by moist air to give oxytrihalides. Such hydrolysis indicates their easily allowing nucleophilic attack. Such hydrolysis is also an indication of a poor base character of the central element (in +5 state) and is also an indication of forming stable multiple metal-oxolinkage. The pentahalides expectedly behave as Lewis acids allowing further coordination by donor ligands such as py, F^-, etc. All these reactions are manifestations of the element using their *d*-orbitals for bonding and hydrolysis. Also note that by virtue of their bigger size niobium and tantalum can assume a coordination number seven as in $[TaF_7]^{2-}$ and $[NbF_7]^{2-}$. These species can be crystallised from solutions of very high fluoride concentration. Structures of NbF_5 and TaF_5 show tetranuclear fluorobridged $[Nb_4F_{20}]$ and $[Ta_4F_{20}]$ species (25-I) (**25.3.1**).

Table 25.3. Halides of Vanadium, Niobium and Tantalum

Element	Fluoride	Chloride	Bromide	Iodide
	VF_5 (white)	—	—	—
Vanadium	VF_4 (brown)	VCl_4 (red-brown)	VBr_4 (majenta)	—
	VF_3 (green)	VCl_3 (violet)	VBr_3 (black)	VI_3 (black)
		VCl_2 (green)		VI_2 (red)
Niobium	NbF_5 (white)	$NbCl_5$ (yellow)	$NbBr_5$ (brown)	NbI_5 (red)
	NbF_4 (black)	$NbCl_4$ (dark)	$NbBr_4$ (dark)	NbI_4 (dark)
Tantalum	TaF_5 (white)	$TaCl_5$ (yellow)	$TaBr_5$ (brown)	TaI_5 (red)
		$TaCl_4$ (dark)	$TaBr_4$ (dark)	TaI_4 (dark)

The tetrahalides of vanadium are obtained by direct interaction of the metal and the halogens. Tetrahalides of niobium and tantalum are generally obtained by the reduction of the pentahalides with the corresponding metal at 300–600°C. Whereas VX_4 are, as expected, paramagnetic, the dark coloured volatile (>300°C) NbX_4 and TaX_4 compounds are diamagnetic. Structure determination shows non-ending octahedral coordination around each Nb or Ta, the equatorial halogens bridging the octahedra. The central atoms of two neighbouring octahedra move close to each other so that spin pairing can occur through direct metal—metal bond. The tetrahalides are hydrolysed to oxydihalides eg: $VOCl_2$, $TaOCl_2$, $NbOCl_2$.

The vanadium trihalides VX_3 are obtained by the action of HX gas on the metal. They crystallise from water as green hexahydrates.

Reduction of NbX_5 and TaX_5 by metals like Cd, Pb at red heat provides complex halides of the type Nb_6Cl_{14}, Nb_6Br_{14}, Ta_6Cl_{14} and Ta_6Br_{14}. On crystallising from warm dilute HCl or HBr they form heptahydrates. Only two of the halogens are immediately precipitated by silver nitrate so that they contain the metal cluster cation $[Nb_6X_{12}]^{2+}$ and $[Ta_6X_{12}]^{2+}$.

Complexes: It is reasonable to expect complex formation to be the highest in +5 state gradually decreasing in the lower oxidation states. However the +5 state being a $3d^{\circ}$ system (no crystal field stabilisation energy being present) and the starting compounds namely vanadate, niobate, etc. having already too strong metal-oxygen bonds, we do not have an extensive series of complexes in this state. Only a few vanadium (V) complexes of the type $M_3{}^1[VO_2\,(\text{oxalate})_2]$, $[VO(OH)\,(\text{bidentate acidato})_2]$ are known. With quadrivalent vanadium extensive studies of complexes have been made. These are of two forms: complexes of oxovanadium (IV) and of non-oxovanadium (IV). Some common examples are $[VCl_6]^{2-}$, $[VO(acac)_2]$, $K_2[VO(oxalate)_2]$, $[VOQ_2]$, $[VO(X)Q_2]$ (QH = quinaldinic acid, X = pyridine, dimetnyl formanide, tetrahydrofuran, etc). Vanadium (III) forms complexes of the type $[V(acac)_3]$, $[VQ_3]$, $[V(oxalate)_3]^{3-}$ etc. However the tendency of complexation by vanadium (III) is far less than that of vanadium (IV). With further reduction in oxidation state we move to π-type complexes, the stabilising ligands being CO, NO, dipyridyl, etc.

Niobium and tantalum have produced only a limited number of complexes. Complexes in the +5 state are restricted mostly to fluoro complexes and some recently studied benzoyl phenylhydroxylamine complexes and hydroxamic acid complexes. Quadrivalent niobium and tantalum halides form complexes of the type $MX_4.2py$. The π-acid complexes are known in $[Nb(dipy)_3]$, $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$.

25.2. OXIDATION STATES OF VANADIUM

25.2.1. Pentavalent Vanadium. Vanadium pentoxide is usually obtained by igniting ammonium vanadate:

$$2NH_4VO_3 \rightarrow V_2O_5+2NH_3+H_2O$$

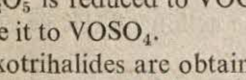
V_2O_5 is also precipitated on the addition of dilute H_2SO_4 to aqueous ammonium vanadate. The pentoxide dissolves in alkalies to give vanadate. At high pH the solution is colourless, the species being mononuclear tetrahedral VO_4^{3-}. As the pH is lowered protonation of the vanadate ion and subsequent polymerisation occurs so that a series of most complicated polynuclear species results: $[VO_2(OH)_3]^{2-}$, $[(VO_2)_2(OH)_5]^{3-}$ and $[(VO_2)_3(OH)_6]^{3-}$. Although vanadium is apparently only 5-coordinate in these species it is doubtless that in aqueous medium they must be adding water to attain six coordination. Again V_2O_5 dissolves in excess acid to give complex species like $[H_2V_{10}O_{28}]^{4-}$, $[HVO_{10}O_{28}]^{5-}$ and $[V_{10}O_{28}]^{6-}$ within the pH range 1.3 to 6.5.

V_2O_5 is reduced to $VOCl_2$ by aqueous HCl. Ethanol and dilute H_2SO_4 together reduce it to $VOSO_4$.

Oxotrihalides are obtained by halogenation of V_2O_3:

$$2V_2O_3+6X_2 \rightarrow 4VOX_3+O_2$$

The oxotrichloride is easily obtained by the action of chlorine on V_2O_5. The oxohalides are easily hydrolysed.

The complexes of pentavalent vanadium are mostly of the dioxo- and oxohydroxo chelate types. Some examples are $M_3^{I}[VO_2(C_2O_4)_2]$, $[VO_2Q.py]$, $[VO(OH)Q_2]$ (QH = quinaldinic acid), $[VO(OH)(RH)_2]$ (RH_2 = benzohydroxamic acid =  $C_6H_5-\overset{O}{\overset{\|}{C}}-NHOH$) etc. All these complexes are diamagnetic ($3d^0$). Although there is no scope for $d-d$ transitions, some vanadium (V) complexes, for example those of the hydroxamates, are coloured intense red-violet due to charge transfer type transition from the reducing ligands to the oxidising vanadium (V). Some of these charge transfer complexes have been made use of in the colorimeteric estimation of trace quantities of vanadium.

25.2.2. Quadrivalent Vanadium. Vanadium (IV) is very well studied. Pentavalent vanadium can be reduced by different reductants to the different oxidation states (Chart 25.1). Reductions with (*a*) alcohol plus H_2SO_4, (*b*) fusion with oxalic acid, (*c*) ferrous ion, (*d*) SO_2 or with (*e*) HI give blue vanadyl salts VOX_2 in solution. The non-oxovanadium (IV) compound VCl_4, for example, is obtained either by the gas phase reaction of $VOCl_3$ with chlorine and charcoal or by the action of chlorine on heated (400°C) vanadium. The tetrachloride readily goes over to $VOCl_2$ in the presence of moist air.

The vanadyl ion is a mild reducing agent being milder than ferrous ion (VO_3^-/VO^{2+}, $E^\circ = 1.0$ volts; Fe^{3+}/Fe^{2+}, $E^\circ = 0.77$ volts). It is not readily oxidised in air. The vanadyl entity is very stable persisting in the solid state, in solution and also in the vapour phase. Vanadium-oxygen (V = O) bond length is very short (1.6A) whereas the other equatorial V—O lengths in $VO(H_2O)_5SO_4$ are ~2.3A. The short bond length indicates multiple bonding. Complex chemistry of vanadyl ion is extensive indeed. Complexes may be cationic ($[VO(dipy)_2Cl]^+$), non-electrolytic ($[VO(acac)_2]$ or anionic $[VO(oxalate)_2]^{2-}$. Vanadium (IV) assumes either a five coordinate square pyramidal structure or a six coordinate octahedral configuration. Many five coordinate species may be easily made to accept a mild donor such as pyridine, tetrahydrofuran, etc. to complete the octahedral geometry:

$$[VOQ_2] \xrightarrow[\text{heat}]{X} [VO(X)Q_2] \; : \quad (QH = \text{quinaldinic acid and}$$

X = pyridine, tetrahydrofuran, thiophene, dimethylformamide, etc.)

Redox Potential	Oxidation State	Species
↑	+5	VO_3^-(colourless)
$E^\circ = 1.0$ volts		(*a*) alcohol+H_2SO_4 (*b*) oxalic acid (*c*) Fe^{2+} (*d*) SO_2 (*e*)[HI ↓
↓ ↑	+4	VO^{2+} (blue)
$E^\circ = 0.3$ volts		(*a*) Sn^{2+} + acid (*b*) SO_2 (*c*) cathodic reduction (bright Pt) (*d*) Ti^{3+} ↓
↓ ↑	+3	V^{3+} (green)
$E^\circ = -0.2$ volts		(*a*) Zn+acid (*b*) cathodic (Pb) reduction (*c*) Cr^{2+} ↓
↓	+2	V^{2+} (violet)

Chart 25.1. Reduction of vanadium (V) io vanadium (IV), (III) and (II).

A very large group of mixed chelates have also been synthesised: [VO(Lut) o-phen)] (Lut H_2 = 2, 6 pyridine dicarboxylic acid), [VO(SB)] (o-phen)] (SBH_2 = tridentate dibasic schiff base). Most oxovanadium (IV) complexes are non-electrolytes and register paramagnetic moments ($3d^1$; 1.6—1.8 B.M.). Only a limited few schiff base complexes of the type, [VO(SB)] (SBH_2 = a tridentate dibasic schiff base, e.g. salicylaldehyde *o*-aminophenol schiff base) have registered low moments (~1.2 B.M.). In these cases dimeric formulation has heen suggested such that two d_{xy} orbitals of the two neighbouring vanadium atoms with one electron on each may overlap allowing partial spin neutralisation.

All non-oxovanadium (IV) complexes are to be synthesised and handled in a moisture-free atmosphere. Complexes such as $[VCl_6]^{2-}$, $VCl_4.(amine)_2$ are known. These are also paramagnetic.

Electronic Spectra: Ideally $[VCl_6]^{2-}$ should give one spin allowed Laporte forbidden transition (d^1 system: $t_{2g} \rightarrow e_g$; ${}^2T_{2g} \rightarrow {}^2E_g$; Chapter 11; page 274) but VCl_4, $(amine)_2$ complexes are under tetragonal distortion since the axial ligand and the equatorial ligand are different. Hence further splitting or flattening of the absorption band is likely.

Oxovanadium (IV) complexes have extremely short V = O bond compared to the other equatorial vanadium-ligand bonds. Such complexes are therefore under tetragonal compression (Fig. 10.15; page 236) such that of the five 3*d* orbitals the d_{z^2} orbital is the most destabilised. The relative ordering of the *d* orbitals is then: $d_{xy} < d_{xz}, d_{yz} < d_{x^2-y^2} < d_{z^2}$. Such complexes should exhibit three *d*–*d* transitions:

$$d_{xy} \rightarrow d_{xz}, d_{yz};\ d_{xy} \rightarrow d_{x^2-y^2};\ d_{xy} \rightarrow d_{z^2}.$$

The second transition gives the value of 10 *Dq*.

There is scope of further splitting of the first transition in very low symmetry complexes. Electronic spectra of some complexes are given in Table 25.4

Table 25.4 Electronic Spectra of Some six Coordinate Vanadium (IV) and oxo-Vanadium (IV) Complexes

Complex	Absorption bands (cm^{-1})
$[VCl_6]^{2-}$	15, 400
$[VF_6]^{2-}$	20,120
$[VO(H_2O)_5]^{2+}$	13, 100; 16,000
[VO (acac)$_2$]	13,030; 17,450; 25,630
[VO (o-phen) (IDA)]	12,500; 17,100; 21,740

25.2.3. Trivalent Vanadium. Quadrivalent vanadium may be further reduced (Chart 25.1) to trivalent vanadium by SO_2, Ti^{3+} or by cathodic reduction (bright platinum electrodes). Reduction is complete when the blue colour of quadrivalent vanadium completely changes to green. Addition of $(NH_4)_2SO_4$ or K_2SO_4 followed by cooling gives green crystals of the alum $NH_4(K)V(SO_4)_2.12H_2O$. This serves as the starting material for the syntheses of many trivalent vanadium complexes. Thus tris (acetylacetonato) vanadium (III) is obtained as red-brown microcrystals by the interaction of acetylacetone and vanadium alum. Tris (quinaldinato) vanadium (III) has been prepared as red-brown powder by the action of quinaldinic acid on tris (acetylacetonato) vanadium (III). Anionic complexes like $[V(C_2O_4)_3]^{3-}$, $[V(CN)_6]^{3-}$ are also known. Interestingly vanadium (III) complexes are not of the oxo-type.

Trichloride and the tribromide can be obtained by passing HCl or HBr gas over the heated metal. These can be crystallised as green hexahydrates from water. The couple VO^{2+}/V^{3+} has $E° = 0.3$ volts so that V^{3+} is a stronger reducing agent than Fe^{2+}(Fe^{3+}/Fe^{2+}, $E° = 0.77$ volts).

All trivalent vanadium compounds are paramagnetic (2 unpaired spins). They are also variously coloured: green, red or brown. Since two unpaired electrons are present several electronic states are possible and *d–d* transitions become complicated and involved.

Electronic Spectra: A d^2 ion in octahedral crystal field can give three spin allowed but Laporte forbidden transitions (Chapter 11; page 274; Fig 11.10); $^3T_{1g}(F) \rightarrow {}^3T_{2g}$; $^3T_{1g}(F) \rightarrow {}^3T_{1g}$ (P); and $^3T_{1g}$ $(F) \rightarrow {}^3A_{2g}$. Hexaaquovanadium (III) has the first two transitions at 17.8 kK and at 25.7 kK. The third transition occurs at 38 kK. The energy gap between $^3T_{2g}$ and $^3A_{2g}$ transitions corresponds to $10Dq$ (Chapter 11; page 274, 277).

25.2.4. Bivalent Vanadium. Vanadyl sulphate is generally reduced to the bivalent stage by zinc and acid till the colour changes through green to violet. It is also obtained by cathodic reduction using a cathode of high hydrogen overvoltage, such as lead. The reduction is best carried out in a diaphragmed cell. A porous pot contains the catholyte—a solution of vanadyl sulphate in dilute H_2SO_4. This pot is inserted into a beaker containing the anolyte—1: 2 dilute H_2SO_4. Cylindrical lead sheet serves as anode as well as cathode. During electrolysis CO_2 is bubbled through. The solution is extremely susceptible to air and has always to be protected by an inert atmosphere. Vanadous sulphate reduces salts of copper, silver, gold, tin and mercury to the corresponding metals. Vanadous sulphate forms a vitriol $VSO_4.7H_2O$ and a series of double sulphates of the schonite type: $M_2^1SO_4.VSO_4.6H_2O$. The vitriol and the double sulphates are isomorphous with corresponding chromous and ferrous compounds. A complex hexacyanide $K_4[V(CN)_6]$ is known. The ability of vanadium (II) to form complexes is very poor.

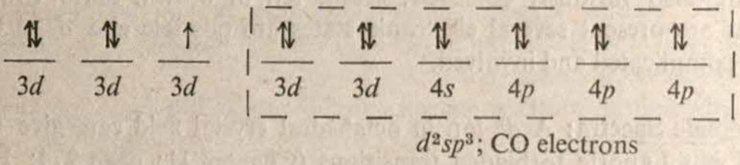
All bivalent vanadium compounds are coloured and are paramagnetic (three unpaired electrons).

Electronic Spectra: Vanadium (II) is a $3d^3$ ion and in an octahedral field it has three spin allowed but Laporte forbidden transition (Chapter 11; page 274):

$$^4A_{2g} \rightarrow {}^4T_{2g};\ {}^4A_{2g} \rightarrow {}^4T_{1g}(F);\ {}^4A_{2g} \rightarrow {}^4T_{1g}\ (P).$$

Vanadous sulphate in aqueous solution shows three absorption bands, at 12.3, 18.5 and 27.9 kK. The $^4A_{2g} \rightarrow {}^4T_{2g}$ transition (12.3 kK) gives the value of $10Dq$ of $[V(H_2O)_6]^{2+}$.

25.2.5. Other low Oxidation States. The unusual oxidation states +1, 0 and −1 are stabilised by π-acid ligands. Zerovalent vanadium found in $V(CO)_6$ is obtained as black crystals by the action of carbon monoxide on finely divided vanadium. The electron number of vanadium in $V(CO)_6$ is just one electron short of the next noble gas (krypton) and the compound is expectedly paramagnetic (one unpaired spin). The six CO groups use d^2sp^3 hybrid orbitals of vanadium so that the five $3d^34s^2$ vanadium electrons are accommodated into the remaining three *d*-orbitals.



Alkaline hydrolysis of the hexacarbonyl produces the carbonylate anion $[V(CO)_6]^-$. This is an intermediate in the synthesis of the hexacarbonyl:

$$VCl_3+CO+Na \xrightarrow[\text{pressure}]{\text{diglyme}} [Na][V(CO)_6] \xrightarrow[\text{then sublime at 50°C}]{H_3PO_4} V(CO)_6$$

Herzog used the following reaction sequences (Chart 25.II) to obtain vanadium (+1), vanadium (0) and vanadium (−1):

$$\begin{tikzcd}
{[V(dipy)_3]I_2} \arrow[r, "\text{Mg or Zn}"] & {[V(dipy)_3]} \arrow[r, "LiAlH_4", "\text{in THF}"'] & {Li[V(dipy)_3].4THF} \arrow[dl, "\text{stoichiometric } I_2"] \\
 & {[V(dipy)_3]I} \arrow[ul, "\text{excess } I_2"] &
\end{tikzcd}$$

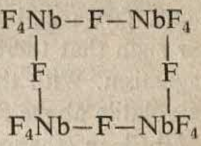
Chart 25.II. Syntheses of dipyridyl complexes of vanadium (+1, 0 and −1).

Since three *d*-orbitals are available to accommodate vanadium outer orbital electrons and since there is room for only one more electron over and above V(0) it follows that the lower limit of oxidation state for vanadium is −1.

25.3. OXIDATION STATES OF NIOBIUM AND TANTALUM

25.3.1. Pentavalent Niobium and Tantalum. $K_8Nb_6O_{19}.16H_2O$ is obtained by fusing Nb_2O_5 and K_2CO_3 in 8:5 ratio and extracting the melt with hot water. After filtering off the unreacted materials the filtrate is treated with a saturated solution of potassium acetate when hydrated potassium hexaniobate crystallises. The hydrated pentoxides are precipitated from solutions of niobates and tantalates on the addition of acids. The hydrated oxides on ignition give the pentoxides Nb_2O_5 and Ta_2O_5. These oxides are rather inert, and can be brought into solution by alkali fusion, bisulphate fusion or by HF. In the first case alkali niobate and tantalate are formed, in the second presumably sulphato complexes and in the third case $[TaF_7]^{2-}$ and $[NbOF_5]^{2-}$. Both niobium and tantalum form polynuclear oxoanions in solutions, such as $[H_2Nb_6O_{19}]^{6-}$, $[HNb_6O_{19}]^{7-}$, $[Nb_6O_{19}]^{8-}$, $[Ta_6O_{19}]^{8-}$ etc.

The pentafluorides are made by fluorination of the metal or of the pentoxides. As mentioned earlier these are volatile covalent compounds (NbF_5, M.P. 80°C, B.P. 235°C; TaF_5, 95°C and 229°C). The species are really tetranuclear Nb_4F_{20} (25-I) and Ta_4F_{20} with four fluorine atoms bridging the four metal atoms situated at the points of a square. The other halides can be obtained by the following general synthetic routes:



(25-I)

$$2Nb + 5I_2 \xrightarrow{300-400°C} 2NbI_5$$

$$Ta_2O_5 + 5C + 5Cl_2 \xrightarrow{400°C} 2TaCl_5 + 5CO$$

$$Ta_2O_5 + 5SOCl_2 \longrightarrow 2TaCl_5 + 5SO_2$$

The halides are readily hydrolysed to $TaOCl_3$, $NbOCl_3$, etc. $NbCl_5$ has been found to be a dimer Nb_2Cl_{10} with two chlorine atoms bridging two octahedra. Halo complexes $[NbF_7]^{2-}$ and $[TaF_7]^{2-}$ can be crystallised from a solution of high F^- concentration.

A series of $M_3[NbOF_6]$ compounds with $M = K^+$, NH_4^+ and Na^+ have been prepared by the interaction of $Nb_2O_5.xH_2O$ with excess MHF_2. Similar reaction with $RbHF_2$ gives $Rb_2[NbOF_5]$ highlighting the fact that the sizes of cations dictate the stabilisation of a particular oxofluoroniobate (V) species. Pyridinium, picolinium, quinolinium and *o*-phenanthrolinium salts of oxotetrafluoroniobates have recently been characterised. The organic base (B) is first acidified with 10% HF solution and then added to a solution of Nb_2O_5 dissolved in minimum volume of 40% HF(Nb_2O_5: B = 1:2). The solution is evaporated till crystallisation of $BH[NbOF_4]$ starts. Guanidinium cation $[BH_2]^{2+}$ seems to stabilise under similar condition oxopentafluoroniobate $BH_2[NbOF_5]$.

Potassium tris (oxalato) niobate, $K_3[NbO(C_2O_4)_3]4H_2O$, has been prepared by dissolving hydrated niobium pentoxide in acidified potassium oxalate and evaporating to crystallisation. This compound reacts with excess KF (4 moles) to furnish crystals of potassium difluoro bis (oxalato) niobate trihydrate, $K_3[NbO(C_2O_4)_2F_2]3H_2O$. The hydrate water is lost over P_2O_5. Molar conductance supports the tri-univalent nature of the complex.

25.3.2. Other Oxidation States. Of the lower oxidation states most informations are available on the quadrivalent state. The pentoxides are reduced to dark grey or black dioxides by hydrogen or carbon at white heat. The dioxides are insoluble in water or acid but dissolve in hot alkali to give alkali niobate and tantalate.

The tetrahalides NbX_4 and TaX_4 have been made by the reduction of the pentahalides by the corresponding metals at 300-600°C. They are diamagnetic although both niobium (IV) and tantalum (IV) are d^1 systems. They form non-ending octahedral structures being bridged on the equatorial plane by halogen atoms. Two metal atoms of neighbouring octahedra move closer to form a close pair such that there may occur a direct metal-metal bonding. This leads to diamagnetism. With the exception of NbF_4 all tetrahalides of niobium and tantalum are volatile above 300°C.

$NbCl_5$ in ethanolic HCl can be reduced electrolytically to pentachloro alkoxo niobium (IV), $[Nb(OR)Cl_5]^{2-}$, isolated as pyridinium salt. This is air sensitive, coloured orange to brown and parmagnetic (one unpaired spin). Other species $[Nb(OEt)_4]_n$, $[NbCl(OEt)_3py_2]_2$ have been reported. These are diamagnetic due to spin-spin interaction.

The pentahalides of niobium $NbX_5(X = Cl, Br, I)$ and TaI_5 are readily reduced by pyridine to $NbX_4.py_2$ and $TaI_4.py_2$. These are non-electrolytes and are paramagnetic (~1.1 B.M.).

It should be noted that no niobium or tantalum complexes of the oxovanadium (IV) type have so far been reported.

Some diarsine complexes of niobium, $NbCl_4$ (diars)$_2$ have been reported. These are presumably eight coordinate being isomorphous with corresponding zirconium (IV) and hafnium (IV) complexes.

The +1 oxidation state of niobium and tantalum is known in the mixed carbonyl—cyclopentadienyl complexes $[C_5H_5M(CO)_4]$ ($M = Nb$ or Ta; $C_5H_6 =$ cyclopentadiene). These are obtained by the oxidation of $[Nb(CO)_6]^-$ or $[Ta(CO)_6]^-$ in presence of sodium cyclopentadienide, NaC_5H_5, by $HgCl_2$:

$$[M(CO)_6]^- + C_5H_5^- + HgCl_2 \rightarrow [C_5H_5M(CO)_4] + 2CO + Hg + 2Cl^-$$

Niobium pentachloride has been reduced in tetrahydrofuran in presence of dipyridyl with lithium to produce violet crystals of $[Nb(dipy)_3]$.

The uninegative state has been stabilised in carbonylate anion $[M(CO)_6]^-$ ($M = Nb, Ta$):

$$MCl_5 + CO \xrightarrow[\text{pressure}]{\text{Na; diglyme}} [M(CO)_6]^-$$

25.4. ISOLATION OF THE GROUP VA ELEMENTS

25.4.1. Vanadium. *Carnotite*, $2K(UO_2)VO_4.3H_2O$ and *vanadinite*, $Pb_5(VO_4)_3Cl$ are the two important ores from which vanadium is extracted. Powdered ore is roasted with sodium chloride whereby sodium vanadate is formed. The roasted material is first leached with water and then with a dilute aqueous acid solution. The combined extract is then treated with H_2SO_4 whereby vanadium is precipitated as V_2O_5. This crude V_2O_5 is redissolved in alkali solution and the soluble vanadate is precipitated as NH_4VO_3 by the addition of NH_4Cl. The pure NH_4VO_3 is next ignited to obtain pure V_2O_5.

Vanadium pentoxide can be reduced by calcium or aluminium. However the control of the reaction temperature becomes difficult. Therefore the metal is now obtained by the reaction of vanadium pentoxide, calcium and iodine in a steel bomb. The iodine combines with calcium at 425°C to form calcium iodide with the release of sufficient energy to start the reduction of V_2O_5 by Ca. The slag consisting of CaI_2 and CaO can be easily removed by water treatment. Very pure vanadium metal may be obtained by the van Arkel–de Boer process (Chapter 24).

25.4.2. Niobium and Tantalum. The elements occur in concentrated forms in ferrous (manganous) tantalates, $Fe(Mn)(TaO_3)_2$, and niobates $Fe(Mn)(NbO_3)_2$. The ores are concentrated by washing and by electromagnetic methods. The concentrated ores containing $\sim 60\%$ or more $Nb_2O_5+Ta_2O_5$ are used in the extraction procedures.

The ore is then fused with sodium hydroxide whereby alkali niobates and tantalates are produced. The fused mass is then leached with hot dilute HCl whereby most of the contaminants iron, manganese and titanium pass into solution leaving behind hydrated pentoxides of niobium and tantalum. The oxides are then treated with HF and KF to form solution of $K_2[NbOF_5]$ and $K_2[TaF_7]$.

Separation of Niobium and Tantalum: Because of similar atomic and ionic sizes of the two elements there is little difference in their chemistries. Charge (+5,) to radius (Nb^{5+}, $Ta^{5+} \sim 0.7$A) ratio is the same in the two cases. Separation is therefore difficult and is based on some slight differences in the solubilities of their compounds or in the differences in their extraction behaviours.

1. *Fractional Crystallisation of Fluoride Complexes:* Solubilities of $K_2[NbOF_5]$ and $K_2[TaF_7]$ in water at 20°C are (in gm/litre) 7.5 and 91.5 respectively. Hence repeated fractional crystallisations will lead to a separation of niobium and tantalum.

2. *Liquid-liquid Extraction:* (*a*) Although fractional crystallisation works well it is not much suitable for large scale separation. In industry large scale separation is achieved by contacting an acidic aqueous solution of $[NbOF_5]^{2-}$ and $[TaF_7]^{2-}$ with methyl isobutyl ketone (MIBK). The tantalum fluoride goes into the organic phase at a low acidity and the niobium oxo-fluoride at a high acidity. Thus by regulating the acidity of the aqueous phase a clean separation of the two elements can be achieved through a few extractions. (*b*) Tantalum is selectively extracted with diisopropyl ketone from a solution $\sim 3M$ in HCl and $0.4M$ in HF. Under this condition niobium is not extracted. (*c*) Niobium is almost quantitatively extracted from aqueous HCl by xylene solution of methyl dioctylamine. Tantalum is not extracted under this condition.

Finally the pure metals may be obtained via electrolysis. For example, electrolysis of fused $K_2[TaF_7]$ at 900°C is carried out in open cast iron pots acting as cathode. Graphite rod suspended into the fused mass serves as the anode. Electrolysis is carried to the extent of 50% of the fluorotantalate being reduced on the cathode surface. The remaining fluorotantalate protects the metal against air at the cell temperature. The fluorotantalate may also be reduced by sodium in steel bombs, On heating the bomb from outside the following exothermic reduction reaction takes place:

$$K_2[TaF_7]+5Na \rightarrow Ta+2KF+5NaF$$

After cooling the contaminants are removed by water treatment.

25.5. USES OF THE GROUP VA ELEMENTS

Vanadium: There are not many industrial applications of pure vanadium metal but *ferrovanadium* has a good demand in steel industry where it serves as component of alloy steels. Ferrovanadium is obtained by the reduction of a component of alloy steels. Ferrovanadium is obtained by the reduction of a mixture of V_2O_5 and Fe_2O_3 with carbon in an electric furnace. The presence of small amounts of vanadium in alloy steels imparts to the steel a higher tensile strength, increased resistance to shock and strain. Vanadium steels are used in high-speed tools, springs, exhaust valves, etc.

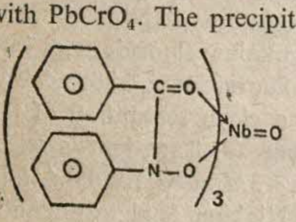
Niobium: Incorporation of about 1% Nb in steel can check deterioration of steel at high temperature. Alloys of high niobium content are useful in making parts of jet planes.

Tantalum: Due to excellent corrosion resistance tantalum finds application in chemical industries in the form of heat exchangers, distilling equipments, aerating devices, corrosion resistant valves, etc. Interestingly tantalum has least foreign body reactions in human body, and therefore finds use in replacing or joining defective parts.

25.6. ANALYTICAL REACTIONS OF THE GROUP VA ELEMENTS

Vanadium: This element is carried as vanadate in the soluble part of group IIIA of the qualitative detection along with aluminium and chromium. This solution is acidified and treated with lead nitrate when $Pb_3(VO_4)_2$ is precipitated along with $PbCrO_4$. The precipitate is dissolved in $3N$ HNO_3, amyl alcohol and H_2O_2 added and shaken. Blue peroxychromic acid appears in the upper layer and a red to redbrown colour of peroxyvanadic acid appears in the lower aqueous layer. The red brown colour is thought to be due to the formation of $[V(-O-O-)]^{3+}$ species.

Mercurous nitrate precipitates vanadate from weakly acid (HNO_3) solution as Hg_3VO_4. This can be ignited to V_2O_5. Vanadium complexes with organic ligands can be directly ignited or ignited under a layer of oxalic acid to V_2O_5



(25–II)

Niobium and Tantalum: N-Benzoyl-N-phenylhydroxylamine (BPHAH) precipitates niobium quantitatively from a tartrate solution of pH 3.5–6.5 as $NbO(BPHA)_3$ (25–II). The tantalum remaining in solution is precipitated at pH 1.5 as $TaO(BPHA)_3$. Both the complexes are ignited to pentoxides and weighed.

A separation of niobium and tantalum has also been achieved by extracting $NbO(BPHA)_3$ into chloroform at pH 4–6. Tantalum is not extracted under this condition.

STUDY QUESTIONS

1. Give a concise resume of the many valences of vanadium.

2. What properties lead to the inclusion of vanadium in group VA instead of group VB of the Periodic Table.

3. Discuss how the properties of vanadium, niobium and tantalum follow from their electronic configurations.

4. Which of the following statements are correct: (*a*) with increasing oxidation state the vanadium oxides become acidic, (*b*) complexing properties of vanadium increases from $+5$ to the $+2$ state, (*c*) vanadium (0), niobium (-1) and tantalum (-1) are found in complexes with π-acid ligands, (*d*) niobium and tantalum are difficultly separable, (*e*) spin paired or low moment compounds are more numerous with vanadium than with niobium and tantalum.

5. Write short accounts of (*a*) vanadyl complexes (*b*) trivalent vanadium (*c*) quadrivalent niobium (*d*) π-acid complexes of vanadium, niobium and tantalum.

6. Describe the extraction and separation of niobium and tantalum.

7. M_2VCl_6 shows one absorption band whereas $[VO(acac)_2]$ and $[VO(H_2O)_5]SO_4$ give multiple bands although all are complexes of quadrivalent vanadium. Explain.

8. Present a comparative account of the electronic spectra of oxovanadium (IV) and oxomolybdenum (V) complexes.

9. What are the likely differences in the electronic spectra of $[V(H_2O)_6]^{3+}$ and $[V(H_2O)_6]^{2+}$ complexes?

10. What type of spectra do you expect in the compound $[VO(OH)(oxin)_2]$ (oxin H= 8-hydroxyquinoline)? Can this spectrum be utlised in colorimetric estimation of the metal (see Chapter 10; page 240).

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26

Group VIA. Chromium, Molybdenum and Tungsten

Chromium, molybdenum and tungsten constitute group VIA of the Periodic Table. Chromium is distributed widely in rocks but only in a few concentrated ores. Virtually all ores of chromium are composed of the mineral *chromite*, $FeCr_2O_4$. Chromium ranks twenty first in the abundance list of the elements. Molybdenum occurs in nature mostly in the form of *molybdenite*, MoS_2, and *wulfenite*, $PbMoO_4$. Tungsten occurs in nature mostly as *wolframite*, $Fe(Mn)WO_4$ and *scheelite*, $CaWO_4$. The relative abundances of the three elements are: Cr(0.02%), Mo (10^{-4}%) and W (10^{-4}%).

26.1. COMPARATIVE STUDY OF THE GROUP VIA ELEMENTS

26.1.1. General Considerations. We would expect for the elements of this group an outer electronic configuration of d^4s^2. Since a half-filled d-subshell imparts a slightly higher stability chromium and molybdenum assume in their atomic state a d^5s^1 configuration. However it will do us no harm if we consider the elements as having d^4s^2 configuration. Their properties are in harmony with their being classified as transition elements. Variable valences, paramagnetism, complex formation are as usual common features of this group.

We have already noted in groups IVA and VA that in a group of transition elements the second and the third members are very close in their properties but the first varies rather widely from the second and the third. One striking evidence of this difference in this group is exhibited in chromium showing its stablest valence in the +3 state whereas this valence is unstable in molybdenum and more so in tungsten. This is also an evidence in favour of the instability of the lower oxidation states in a group with increasing atomic number. The valences exhibited by the elements range from the group valence +6 down to 0:

Chromium	+6	+5	+4	**+3**	+2	+1	0
Molybdenum	**+6**	+5	+4	+3	+2	+1	0
Tungsten	**+6**	+5	+4	+3	+2	+1	0

The valence +6 is the highest for all these elements. It is also the stablest for molybdenum and tungsten but not for chromium. Note that the +6 state results from the use of all the five 3*d* and 1*s* electrons. Since with chromium the +3 state is the commonest and the stablest it follows that higher-valent chromium compounds particularly those of the +6 valence will be strong oxidants. In fact they are. Molybdenum and tungsten show no oxidising properties in the +6 state since this is their commonest and stablest state. But molybdenum (III) and tungsten (III) are strongly reducing, but chromium (III) is not.

It is natural to expect that in the group valence, as high as +6, the elements will form only covalent compounds. Cations (basic properties) will appear only in the lower valences. Thus chromium (III) is ionised but chromium (VI) is covalent. Similarly molybdenum and tungsten form aquo or complex cations but not earlier than the +3 state.

As a general rule higher oxides become acidic and the lower ones basic, and also that oxidation state remaining the same, acidity falls with increasing atomic number. The acidity of the H_2XO_4 compounds falls in the order Cr>Mo>W. Again CrO_3 is acidic, $Cr(OH)_3$ is amphoteric but $Cr(OH)_2$ is wholly basic.

Table 26.1 and Table 26.2 record the electronic configurations, ionisation potential, electronegativity, atomic and ionic radii. etc. Typical of other groups of transition elements the ionisation potential and electronegativity change but little in the series Cr—Mo—W. Molybdenum and tungsten have similar atomic and ionic radii but the atomic weight of tungsten (184) is almost double that of molybdenum (10.4) to tungsten (19.3).

Table 26.1. Electronic Configurations and Some Properties of Group VIA Elements

Element	Atomic Number	Electronic Configuration	Ionisation Potential (*ev*)	Electro-negativity
Chromium	24	[Ar] $3d^5 4s^1$	6.76, 16.49, 30.95	1.6
Molybdenum	42	[Kr] $4d^5 5s^1$	7.10, 16.15, 27.13	1.8
Tungsten	74	[Xe] $4f^{14} 5d^4 6s^2$	7.98, 17.7	1.7

Table 26.2. Some More Properties of Group VIA Elements

Element	Atomic Radius (A)	Ionic Radius (A) (M^{6+})	M.P. (°C)	B.P. (°C)	Density (gm/ml)
Chromium	1.27	0.52	1875	2199	7.1
Molybdenum	1.39	0.62	2610	5560	10.4
Tungsten	1.39	0.67	3410	5900	19.3

26.1.2. Chemical Behaviour. *Hydrides:* The hydrides are of the interstitial type and of uncertain composition, for example $CrH_{1\cdot7}$.

Oxides and Oxyacids: The hexavalent oxides CrO_3, MoO_3 and WO_3 are well known. These are precipitated from alkali chromates, molybdates and tungstates respectively by the addition of acids, and then igniting H_2MoO_4 and H_2WO_4 to the oxides. The metals may also be ignited in oxygen or air to give the oxides. All the oxides are acidic and dissolve in alkali to give chromates, molybdates and tungstates. Trivalent $Cr(OH)_3$ is precipitated as a green material from a chromic solution. This hydroxide is amphoteric, dissolving in acids to give chromic salts, and in alkalies to give chromites such as $NaCrO_2$. Brown coloured $MoO(OH)_3$ is precipitated from molybdenum (V) solutions on the addition of ammonia. This dissolves in acids. A few lower oxides, such as MO_2 and WO_2 obtained by the reduction of trioxides with hydrogen, are also known. The acidic nature of the oxides decreases with decreasing valence.

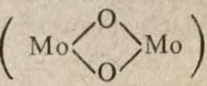
Halides: With high oxidation number the halides are expectedly covalent. Thus MoF_6 and WF_6 are low boiling (B. P. 35°C and 17°C respectively), non-electrolytic, diamagnetic and extremely susceptible to hydrolysis. Interestingly SF_6 of group VIB is very inert to hydrolysis, presumably because sulphur has a maximum coordination number six but molybdenum and tungsten may go upto eight and hence a nucleophilic attack by H_2O is facilitated. WCl_6 is also volatile, monomeric, soluble in organic solvents and hydrolysed to tungstic acid. $MoCl_5$ (M.P. 194°C, B.P. 628°C) is monomeric in the vapour state but is a chlorine bridged dimer in the crystalline state. The lower halides have very complicated structures. For example, $MoCl_2$ is really $[Mo_6Cl_8]Cl_4$, an example of metal cluster compounds. WCl_2 is likely to be similar. The higher halides are obtained by direct halogenation of the metals. The lower halides are obtained by the reduction of the higher halides with metal or hydrogen under optimum temperature, pressure and time. Sometimes some other metals such as aluminium may be used to arrest the liberated halogen. Table 26.3 lists some fluorides and chlorides.

Table 26.3. Fluorides and Chlorides of Chromium, Molybdenum and Tungsten

Element	Oxidation Number				
	+6	+5	+4	+3	+2
Chromium	— —	CrF_5 red	CrF_4 green back	CrF_3 green $CrCl_3$ red violet	CrF_2 green $CrCl_2$ blue
Molybdenum	MoF_5 colourless	MoF_5 yellow $MoCl_5$ green black	MoF_4 green $MoCl_4$ dark red	MoF_3 yellow brown $MoCl_3$ dark red	— — $MoCl_2$ yellow
Tungsten	WF_6 colourless WCl_6 blue black	— WCl_5 green black	WF_4 red brown WCl_4 black		WCl_2 grey

All the three elements form large number of oxyhalides. Chromyl chloride CrO_2Cl_2 is well known since it serves as a distinctive test for chloride ion but not for covalent chloride. The corresponding bromide and iodide are not formed presumably because chromium (VI) is much too strong an oxidant. The fluoride is formed in poor yield. The volatile nature of CrO_2Cl_2 points to its covalent character. But the corresponding molybdenum compound MoO_2Cl_2 ionises in solution to MoO_2^{2+} and Cl^+ ions.

Complexes: Complexes of higher-valent chromium are little known presumably because of the great oxidising power of the $+6$ state. In the $+3$ state chromium has an enormous power of complex formation almost comparable to the power of cobalt (III). In fact much of Werner's pioneering works on coordination complexes centred around cobalt (III) and chromium (III). All these complexes are paramagnetic (d^3 system, $\mu \sim 3.9$ B.M.). Bivalent chromium has also been stabilised by complexation. Still lower oxidation states are stabilised by π-acid ligands, such as carbon monoxide, dipyridyl, benzene, etc.

Both molybdenum (VI) and tungsten (VI) form tetrahedral monomeric MO_4^{2-} anions in alkaline medium. On acidification of the molybdate and tungstate solutions the anions polymerise and give condensed polyacids. Both these oxidation states can give rise to complexes, these being of the dioxomolybdenum (VI) $(O = Mo = O)$ and dioxotungsten $(O = W = O)$ types. Pentavalent molybdenum complexes are mostly of the molybdenyl $\left(Mo = O \right)$ or  type.

As in oxovanadium (IV) complexes, there is a strong molybdenum—oxygen double bond which persists in solution and also in the solid state. Some common examples are $[MoOCl_5]^{2-}$, $[MoOCl(acac)_2]$, etc. Many of the oxo-molybdenum (V) complexes are diamagnetic due to pairing of spins of the two neighbouring molybdenum (V). Quadrivalent molybdenum complexes are both of the oxo- and non-oxotype although a limited few are known. Trivalent molybdenum complexes are of the Mo^{3+} cation and are not of the oxomolybdenum type. Note the similarities with vanadium complexes. Molybdenum (III) complexes are paramagnetic with three unpaired spins.

Tungsten complexes in lower oxidation states are less stable than the corresponding molybdenum complexes. Where these are known they are of the type of the corresponding molybdenum complexes. Extremely low oxidation states are stabilised by π-acid ligands e.g.: $[Mo(CO)_6]$, $[Mo(C_6H_6)_2]$, $[W(C_6H_6)_2]$, etc.

26.2. OXIDATION STATES OF CHROMIUM

26.2.1. Hexavalent Chromium. The important compounds that exemplify this oxidation state are CrO_3, chromates and dichromates, chromyl chloride and peroxychromates.

Chromium Trioxide: This is obtained as scarlet needles on treating a concentrated solution of a dichromate with cold concentrated H_2SO_4:

$$K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + 2CrO_3 + H_2O$$

The crystals of CrO_3 are filtered on sintered glass funnel, washed with HNO_3 and then dried at 60°C in a stream of air to remove the nitric acid. The trioxide is readily soluble in water giving chromic acid H_2CrO_4. On heating above its melting point 196°C it decomposes into Cr_2O_3 and O_2. It is a powerful oxidant:

$$2CrO_3+3SnCl_2+12HCl \rightarrow 2CrCl_3+3SnCl_4+6H_2O$$
$$4CrO_3+3As_2O_3+12HCl+3H_2O \rightarrow 4CrCl_3+6H_3AsO_4$$
$$2CrO_3+3H_2S+3H_2SO_4 \rightarrow Cr_2(SO_4)_3+3S+6H_2O$$

Chromium trioxide is used in many organic syntheses.

Sodium and Potassium Dichromates: Sodium dichromate is commercially prepared by roasting chromite ore with sodium carbonate and lime in the presence of air:

$$4FeCr_2O_4+8Na_2CO_3+7O_2 \rightarrow 2Fe_2O_3+8Na_2CrO_4+8CO_2$$

The lime helps in keeping the mass porous. The roasted mass is extracted with water and treated with sulphuric acid to convert the chromate to dichromate:

$$2Na_2CrO_4+H_2SO_4 \rightarrow Na_2Cr_2O_7+Na_2SO_4+H_2O$$

The sodium dichromate solution, on treatment with KCl, precipitates the less soluble $K_2Cr_2O_7$.

The dichromate ion in basic solution changes to the tetrahedral chromate ion which is isomorphous with the sulphate ion. On lowering the pH the yellow chromate goes over to the orange dichromate:

$$CrO_4^{2-}+H^+ \rightarrow CrO_3(OH)^-;\ 2CrO_3(OH)^- \rightarrow H_2O+Cr_2O_7^{2-}$$

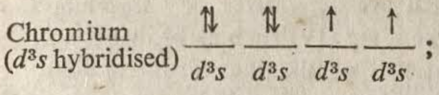
A neutral aqueous solution of a dichromate or a chromate is an equilibrium mixture of $Cr_2O_7^{2-}$ and CrO_4^{2-} ions. Addition of H^+ shifts the equilibrium towards $Cr_2O_7^{2-}$, and of OH^- ions towards CrO_4^{2-} ions. Interestingly addition of lead acetate to an aqueous solution of $K_2Cr_2O_7$ precipitates $PbCrO_4$ rather than $PbCr_2O_7$. This is due to the solubility product of $PbCrO_4$ being much smaller than that of $PbCr_2O_7$ so that the entire equilibrium is shifted to the chromate side.

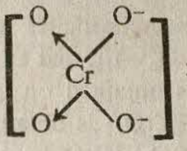
Potassium dichromate in acid solution is a very strong oxidant. The E° of the $Cr_2O_7^{2-}/Cr^{3+}$ couple is +1.33 volts whereas that of MnO_4^-/Mn^{2+} is +1.51 volts. Although it is not as strong an oxidant as permanganate and although it cannot serve as its own indicator it has some advantages, however; it can be used as a primary standard, and can be used in HCl medium. Some of the common oxidising reactions are:

$$K_2Cr_2O_7+6FeSO_4+7H_2SO_4 \rightarrow Cr_2(SO_4)_3+3Fe_2(SO_4)_3+K_2SO_4+7H_2O$$
$$K_2Cr_2O_7+6KI+7H_2SO_4 \rightarrow Cr_2(SO_4)_3+4K_2SO_4+3I_2+7H_2O$$

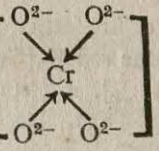
Note the E° of the CrO_4^{2-}/Cr^{3+} couple is −0.13 volts so that chromate ion is not an oxidant.

In sulphate ion (Chapter 19) we have seen that sp^3 hybrid orbitals of sulphur are used. Two of these sp^3 hybrid orbitals have two pairs of electrons which are donated to two oxygen atoms forming two coordinate links. The other two sp^3 hybrid orbitals each having one electron overlap with appropriate orbitals of O^- ions with unpaired electron. Here chromium utilises three of its *d*-orbitals namely $3d_{xy}$, $3d_{xz}$ and $3d_{yz}$ and the $4s$ orbital to form a set of equivalent tetrahedral d^3s orbitals. Both sp^3 and d^3s give tetrahedral hybrid orbitals. Note that $4s4p^3$ hybridisation is less likely in this case because the $4p$ orbitals are of higher energy than the $3d$ orbitals. The structure may be represented as (26–I):





(26-I)



(26-II)

There is scope for double bond formation via overlap of filled oxygen orbitals with empty $3d$ or $4p$ orbitals of chromium. All the bonds become equivalent through resonance. Alternatively we may conceive chromium (VI) as a $3d^0$ system. The six electrons of chromium and two from the charge-neutralising cations now distribute over the four oxygen making them O^{2-} ions. A filled p orbital of each oxide ion then makes a coordinate link to chromium (VI) (26-II). Scope of double bonding remains. The chromium–oxygen bond length has been found to be around 1.67A (cf: $V = O$ in oxo-vanadium (IV) complexes: 1.67A).

Chromyl Chloride: This is obtained as a deep red liquid by the action of HCl on CrO_3 or by warming potassium dichromate with alkali chloride in concentrated H_2SO_4:

$$CrO_3 + 2HCl \rightarrow CrO_2Cl_2 + H_2O$$

$$K_2Cr_2O_7 + 4KCl + 3H_2SO_4 \rightarrow 2CrO_2Cl_2 + 2K_2SO_4 + 3H_2O$$

This latter reaction is a basis of the qualitative detection of chloride ion. Chromyl chloride test is a test for ionic chloride, and hence chlorides of mercury do not respond to this test due to their poor ionisation. Chromyl chloride is hydrolysed by water to chromic acid and HCl. It is a covalent compound.

Peroxychromates: On the addition of H_2O_2 to an acid (H_2SO_4) solution of a chromate or a dichromate a blue colour is produced, which can be extracted into ether. This serves as a test of chromium. The ether extract is believed to be an unstable addition compound of ether and peroxychromium: $(C_2H_5)_2O \rightarrow CrO_5$. Earlier the blue compound used to be formulated as $HCrO_5$ rather than CrO_5. Several lines of evidences point to the latter formula. Thus dilute acids liberate 7 atoms of active oxygen per two moles of the peroxy compound rather than 6 atoms of active oxygen as would be expected from $HCrO_5$ formulation ($2CrO_5 \rightarrow Cr_2O_3 + 7O$; $2HCrO_5 \rightarrow Cr_2O_3 + H_2O + 6O$). Titration with $KMnO_4$ in acid medium shows that the molecule has two peroxy groups as it consumes four equivalents of permanganate:

$$CrO_5 + 2H_2O \rightarrow CrO_3 + 2H_2O_2$$

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

(Note 1 mole H_2O_2 = 2 equivalents of $KMnO_4$)

The structure of CrO_5 is thus $CrO(-O_2-)_2$. The etheral blue solution gives on treatment with pyridine a monomeric, diamagnetic and benzene-soluble adduct; $py \rightarrow CrO(-O_2-)_2$. Structure determination shows that the molecule is a pentagonal pyramid (not an octahedron) with the oxide oxygen at the apex.

There are other peroxychromates which are derivatives of chromium (V) such as the red $K_3[Cr(-O_2-)_4]$, and of chromium (IV) such as brown $[(NH_3)_3$-$Cr(-O_2-)_2]$. K_3CrO_8 is obtained on treatment of alkaline chromate solution with 30% H_2O_2. $[(NH_3)_3CrO_4]$ is obtained as brown crystals by heating to 50° the solution containing $(NH_4)_3[CrO_8]$.

Electronic Spectra: Hexavalent chromium may be viewed as a $3d^0$ system. Hence it can have no $d-d$ transition. The yellow colour of potassium chromate is due to charge transfer transition from M.O.'s which are predominantly oxide orbitals to M.O.'s which are predominantly chromium $3d$. This absorption ($2p \rightarrow 3d$) is Laporte allowed and is therefore very intense ($\lambda_{max} = 370$ nm; $\epsilon = 4808$) (cf: Chapter 10; page 240).

26.2.2. Pentavalent Chromium. Compounds of chromium (V) are little known. $CrOCl_3$ can be made by the reduction of CrO_2Cl_2. Oxochloro compounds $M_2{}^I[CrOCl_5]$ are obtained by the reduction of CrO_3 with concentrated HCl in the presence of alkali ions at 0°C. These are blue black, hygroscopic solids with paramagnetic moments ($3d^1$ system). CrF_5 is a red liquid (M.P. 30°C) obtained by the interaction of fluorine and the metal at high temperature and pressure. Peroxo complexes have been mentioned under peroxychromates.

26.2.3. Quadrivalent Chromium. Tetrahalides CrF_4, $CrCl_4$, and $CrBr_4$ are known. Of these CrF_4 has been obtained as dark green-black paramagnetic ($\mu = 3.0$ B.M.) solid by the action of fluorine on CrF_3. MF salts react with CrF_4 in 1:1 ratio in BrF_3 solvent giving paramagnetic ($\mu = 3.1$ B.M.) complexes $M^I[CrF_5]$. $CrCl_4$ and $CrBr_4$ exist in the vapour state when the trichloride and the tribromide are heated with the respective halogens. A peroxy complex $[(NH_3)_3Cr(-O_2-)_2]$ has already been referred to under peroxychromates.

26.2.4. Trivalent Chromium. This is the stablest oxidation state of chromium and a large number of compounds and, in particular, complexes are known. Like cobalt (III), chromium (III) complexes are also kinetically inert and undergo substitution reactions at a measurable rate. It has a consistent coordination number six. It should be recalled that a d^3 ion has a high CFSE (-12 Dq) in octahedral geometry. All chromium (III) compounds are paramagnetic ($3d^3$ system), and assume different colours depending on the strength of the coordinating ligands. Typical of trivalent cations it forms alums with monovalent metal sulphates. Like ferric and aluminium salts, chromic salts are widely used as mordants.

Chrome green: This is in fact ignited chromic oxide (Cr_2O_3). It has a very high melting point and is very refractory. It may be obtained by heating $Cr(OH)_3$ or $(NH_4)_2Cr_2O_7$:

$$2Cr(OH)_3 \rightarrow Cr_2O_3+3H_2O$$
$$(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3+N_2+4H_2O$$

It may be fused with $KHSO_4$ to give soluble $Cr_2(SO_4)_3$ or with Na_2O_2 to give Na_2CrO_4.

Chrome green is used as a pigment in decorating glass and porcelain wares. The compound is used as a green oil paint under the name *chrome green.*

Chromic Chloride: Anhydrous $CrCl_3$ is obtained by the action of chlorine on the metal or on a mixture of Cr_2O_3 and carbon. It can be purified by sublimation. It can also be obtained by dehydrating the hydrated chloride with $SOCl_2$ under reflux:

$$[Cr(H_2O)_6]Cl_3+6SOCl_2 \rightarrow CrCl_3+12HCl+6SO_2$$

Anhydrous $CrCl_3$ is insoluble in water and alcohol. However it reacts in presence of complexing agents. An interesting series of hydrate and ionisation isomers are known with chromic chloride. These isomers may have 0, 1, 2 or all 3 chlorine atoms ionised with 3, 4, 5 or $6H_2O$ molecules being present in the coordination sphere so as to maintain six coordination. In presence of a trace of chromous chloride ($CrCl_2$), the anhydrous $CrCl_3$ dissolves readily in water wherefrom a dark green $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ crystallises. Silver nitrate precipitates only a third of the entire chlorine. This variety can also be made by dissolving chromic hydroxide in HCl and evaporating till the weight corresponds to $CrCl_3.6H_2O$ and then allowing to crystallise.

When the dark green variety is dissolved in its own weight of water, boiled under reflux for half an hour, cooled below 0°C and treated with HCl gas, a grey blue isomer $[Cr(H_2O)_6]Cl_3$ crystallises. All its three chlorine atoms are precipitated by silver nitrate.

When the filtrate from the above grey-blue isomer is treated with HCl-gas-saturated ether and then further treated with HCl gas at 10°C, a light green variety $[Cr(H_2O)_5Cl]Cl_2.H_2O$ crystallises. A fresh solution of this variety gives with silver nitrate only two moles of AgCl. Furthermore, with $[PrCl_6]^{2-}$ a precipitate of $[Cr(H_2O)_5Cl]\ [PtCl_6].5H_2O$ is obtained.

A non-ionised $[CrCl_3(H_2O)_3]$ was prepared by Recoura. This compound gives a brown solution in ether. In alcohol it reacts slowly with silver nitrate. Water at once converts it to the common dark green variety $[Cr(H_2O)_4Cl_2]Cl.2H_2O$.

Chrome Alum: Chromium (III) sulphate forms alum type double sulphate with alkali metal sulphate. *Chrome alum*, $K_2SO_4.Cr_2(SO_4)_3.24H_2O$ [or $KCr(SO_4)_2.12H_2O$] is generally obtained by the reduction of $K_2Cr_2O_7$ in presence of sulphuric acid by SO_2 or by alcohol, the latter being oxidised to aldehyde:

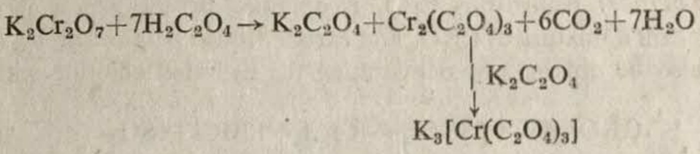
$$K_2Cr_2O_7+H_2SO_4+3SO_2 \rightarrow K_2SO_4+Cr_2(SO_4)_3+H_2O$$

The substance crystallises in beautiful octahedra of violet colour.

Chromium (III) Complexes: The complexes may be cationic, anionic or neutral. Many of the complexes have been resolved into optical isomers. The complexes have a coordination number six, and are paramagnetic ($\mu \sim 3.9$ B.M.).

Reinecke's Salt, $NH_4[Cr(NH_3)_2(NCS)_4].H_2O$: This is prepared by adding $(NH_4)_2Cr_2O_7$ slowly to fused ammonium thiocyanate. The red product is recrystallised from alcohol. It has a *trans* diammine configuration and is a uni-univalent electrolyte. This is widely used to precipitate large cations. The thiocyanato groups are linked through nitrogen so that the complex is really a *trans* diammine tetrakis (isothiocyanato) chromate (III).

Potassium tris (oxalato) Chromate (III): This is obtained by reducing $K_2Cr_2O_7$ with oxalic acid and then adding more potassium oxalate:

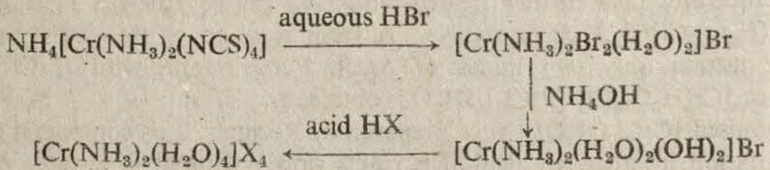


$$\begin{tikzcd} K_2Cr_2O_7+7H_2C_2O_4 \arrow[r] & K_2C_2O_4+Cr_2(C_2O_4)_3+6CO_2+7H_2O \arrow[d, "K_2C_2O_4"] \\ & K_3[Cr(C_2O_4)_3] \end{tikzcd}$$

This forms blue crystals. The compound was resolved into optical isomers by Werner.

Chromium (III) Ammines: A very large number of ammine complexes are known beginning with the hexammine $[Cr(NH_3)_6]X_3$ through $[Cr(NH_3)_3X_3]$ to $M[Cr(NH_3)_2X_4]$ (X = halide ion). The coordination zone may also have other neutral donors alongside a few NH_3 groups. The hexammine salts can be made by the action of liquid ammonia on anhydrous chromic chloride or by the action of ammonia and air on a chromous solution. Hexaaquo chromic ion reacts very sluggishly with ammonia. The aquopentammine and the diaquotetrammine salts are obtained by the aquation of the hexammine complex. The tetrammine complexes can give rise to *cis*- and *trans*-isomers.

If the monodentate group is also ambidentate in character further scope of linkage isomerism occurs. The diammine tetraquo complexes have been obtained by the following sequence:



$$\begin{tikzcd} NH_4[Cr(NH_3)_2(NCS)_4] \arrow[r, "\text{aqueous HBr}"] & {[Cr(NH_3)_2Br_2(H_2O)_2]Br} \arrow[d, "NH_4OH"] \\ {[Cr(NH_3)_2(H_2O)_4]X_4} & {[Cr(NH_3)_2(H_2O)_2(OH)_2]Br} \arrow[l, "\text{acid HX}"'] \end{tikzcd}$$

Tris (acetylacetonato) Chromium (III): This is obtained by heating freshly prepared $Cr(OH)_3$ with acetylacetone. It is a non-electrolytic purple solid melting at 214°C and boiling undecomposed at 340°C.

Tris (biguanide) Chromium (III): Dropwise addition of an aqueous chrome alum solution to a hot, strongly alkaline solution of biguanide (BigH) gives crimson red crystals of $[Cr(Big)_3].H_2O$. This can be neutralised with acids HX to give orange-coloured salts $[Cr(BigH)_3]X_3$ (cf. page 187, Part I). The chloride salt readily reacts with chosen bidentate ligands like picolinic acid (PicH), o-phenanthroline, etc-to furnish mixed chelates of the type $[Cr(Pic)\cdot(BigH)_2]X_2$, $[Cr(o\text{-}phen)(BigH)_2]X_3$ etc.

Electronic Spectra: $3d^3$ chromium (III) has three spin allowed but Laporte forbidden transitions in an octahedral field (Chapter 11; page 274): ${}^4A_{2g}\rightarrow{}^4T_{2g}$; ${}^4A_{2g}\rightarrow{}^4T_{1g}(F)$; ${}^4A_{2g}\rightarrow{}^4T_{1g}$ (P). Some examples are given in Table 26.4. The spectrum of the hexaaquo complex is given in Fig. 26.1. The lowest energy ${}^4A_{2g}\rightarrow{}^4T_{2g}$ transition (17.4 kK) gives 10 Dq.

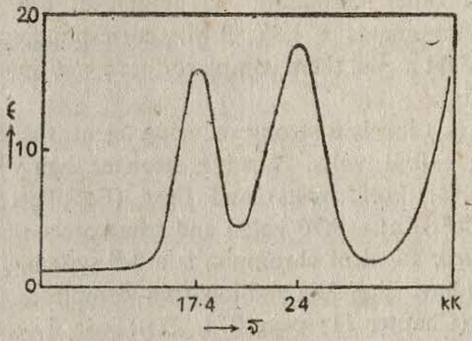


Fig. 26.1. Spectrum of $[Cr(H_2O)_6]^{3+}$

Table 26.4. Electronic Spectra of some Six-coordinate Chromium (III) Complexes

Complex	${}^4A_{2g}\rightarrow{}^4T_{2g}$	${}^4A_{2g}\rightarrow{}^4T_{1g}$(F)	${}^4A_{2g}\rightarrow{}^4T_{1g}$(P)
$[Cr(H_2O)_6]^{3+}$	17.4 kK	24.6 kK	37.8 kK
$[CrF_6]^{3-}$	14.9	22.7	34.4
$[Cr(NH_3)_6]^{3+}$	21.55	28.5	—
$[Cr(en)_3]^{3+}$	21.8	28.45	—
$[Cr(BigH)_3]^{3+}$	20.8	—	—
$[Cr(o\text{-}phen)(BigH)_2]^{3+}$	21.3	—	

26.2.5. Bivalent Chromium. Chromium (III) can be reduced with Zn and HCl to the sky blue coloured chromium (II) ion. It is also obtained by dissolving chromium metal in acid solution. Excluding air it is possible to crystallise several salts: sulphate ($5H_2O$), chloride ($4H_2O$), bromide ($6H_2O$) and acetate (H_2O). Of these the acetate alone is red coloured and is air-stable when dry. For the synthesis of chromous acetate chromium (III) is first reduced with Zn and HCl to sky blue chromium (II). This solution is then run into a saturated aqueous solution of sodium acetate. The precipitated red $Cr(CH_3COO)_2H_2O$ is then filtered, preferably in an atmosphere of H_2 or N_2, washed with ether and dried in a desiccator. It is a good starting material for the syntheses of other chromium (II) complexes. The acetate is a dimer with strong metal—metal bonding resulting in spin pairing (cf: 29-III). All the other salts are blue, monomeric and paramagnetic (4 unpaired spins). Stable complexes with hydrazine $CrCl_2.2N_2H_4$ and

$CrI_2.2N_2H_4$ have also been obtained. The following octahedral ionic complexes are also known: $[Cr(dipy)_3](ClO_4)_2$ (black violet) ; $K_4[Cr(CN)_6]$ (blue); $K_4[Cr(NCS)_6]$ (dark blue). As expected for *inner orbital* complex (d^2sp^3 hybridisation) the cyano complex has a magnetic moment of ~3.1 B.M. (two unpaired electrons). In crystal field language we call the cyano complex to possess *low spin* t_{2g}^4 configuration. All other chromium (II) complexes are *outer orbital* (sp^3d^2 hybridisation) with moments ~4.85 B.M. corresponding to four unpaired spins. On crystal field model these complexes have *high spin* $t_{2g}^3e_g^1$ configuration (Chapters 10 and 11).

The chromium (II) ion is a strong reducing agent, the $E°$ value of the Cr^{3+}/Cr^{2+} couple being -0.41 volts. Thus it is stronger than V^{2+}(V^{3+} V^{2+}; $E°, -0.26$ volts), Sn^{2+}(Sn^{4+}/Sn^{2+}; $+0.15$ volts) and Fe^{2+} (Fe^{3+}/Fe^{2+}; $+0.77$ volts) but weakre than Zn (Zn^{2+}/Zn; -0.76 volts) and some other metals.

Electronic Spectra: Bivalent chromium is a $3d^4$ system. Depending on crystal field strength it can have high-spin and low-spin complexes. The following transitions are possible (Chapter 11; page 274, 275):

high-spin : only ${}^5E_g \rightarrow {}^5T_{2g}$
low-spin : ${}^3T_{1g} \rightarrow {}^3E_g$; ${}^3T_{1g} \rightarrow {}^3T_{2g}$; ${}^3T_{1g} \rightarrow {}^3A_{1g}$, etc.

Most chromium (II) high spin octahedral complexes have a broad band around 13–17 kK. No data are available for low-spin complexes.

26.2.6. Other Low Oxidation States. Reduction of air-free solution of $[Cr(dipy)_3]$ $(ClO_4)_2$ with magnesium in the presence of NH_4ClO_4 gives sparingly soluble blue coloured $[Cr(dipy)_3]ClO_4$. Further reduction of $[Cr(dipy)_3]^+$ by sodium in tetrahydrofuran gives dark red powder of $[Cr(dipy)_3]$. It bursts into flame in air. Zerovalent $[Cr(CO)_6]$ is known as colourless air-stable crystals obtained by the action of CO on anhydrous $CrCl_3$ in the presence of a reducing agent such as triethylaluminium in ether. A monovalent complex, bis (benzene) chromium (I) was synthesised by Fischer by heating (140°C) under pressure a mixture of $CrCl_2$, $AlCl_3$, benzene and aluminium powder (as halogen acceptor) when the following reaction occurred:

$$3CrCl_2+2Al+6C_6H_6+AlCl_3 \rightarrow 3[Cr(C_6H_6)_2]\ [AlCl_4]$$

The paramagnetic $[Cr(C_6H_6)_2]^+$ was then reduced to dark brown, diamagnetic $[Cr(C_6H_6)_2]$ by sodium dithionite and the compound purified by sublimation.

$$2[Cr(C_6H_6)_2]^+ + S_2O_4^{2-} + 4OH^- \rightarrow 2[Cr(C_6H_6)_2] + 2H_2O + 2SO_3^{2-}$$

Substitution reaction by o-phenylenebisdimethylarsine (diars) on $[Cr(CO)_6]$ gave $[Cr(CO)_2\,(diars)_2]$.

Chromium (II) acetate suffers disproportionation when an alcoholic suspension of the compound is treated with an excess of arylisocyanide:

$$3Cr^{2+} + 18CNR \rightarrow [Cr(CNR)_6] + 2[Cr(CNR)_6]^{3+}$$

Hexa (arylisocyanide) chromium (0) compounds are diamagnetic, yellow to red crystalline substances. These are stable to air, soluble in chloroform and benzene but sparingly so in alcohol.

26.3. OXIDATION STATES OF MOLYBDENUM AND TUNGSTEN

26.3.1. Hexavalent Molybdenum and Tungsten. Free molybdic acid $H_2MoO_4.H_2O$ precipitates from a solution of a molybdate in concentrated HNO_3. On ignition this gives MoO_3. This, however, is not the anydride of molybdic acid since MoO_3 does not generate H_2MoO_4 on treating with water. The oxide is acidic and with alkalies gives molybdate. Tungstic acid hydrate $H_2WO_4.H_2O$ is similarly precipitated from a tungstate solution on acidification. On ignition WO_3 is obtained. This also is not the anhydride of tungstic acid. However it dissolves in alkalies to produce tungstates.

Reduction of molybdic acid or tungstic acid or of their trioxides by zinc, SO_2 or other reducing agents often gives blue or blue black products. These are often called *molybdemum blue* or *tungsten blue.* Their structures are not well established but they are believed to contain both +5 and +6 oxidation states. Some typical compositions are: $MoO_{2\cdot5}(OH)_{0\cdot5}$; $MoO_{2\cdot88}\,H_2O$; $WO_{2\cdot67}(OH)_{0\cdot33}$.

Both molybdic acid and tungstic acid have enormous power of condensation and polymerisation not only with their own acids but with other acids as well. When a strongly basic solution containing the tetrahedral molybdate ion $[MoO_4]^{2-}$ is acidified the molybdate ion undergoes condensation in steps to give polymolybdate ions such as $[Mo_7O_{24}]^{6-}$:

$$7MoO_4^{2-}+8H^+ \rightarrow [Mo_7O_{24}]^{6-}+4H_2O$$

When MoO_3 is dissolved in excess of hot concentrated ammonia $(NH_4)_2[MoO_4]$ crystallises but from a near-neutral solution ammonium paramolybdate $(NH_4)_6[Mo_7O_{24}].4H_2O$ separates. The behaviour of alkali tungstate towards acids is also complicated and numerous polytungstates exist at different acid range. Some typical forms are: $[HW_6O_{21}]^{5-}$, $[W_{12}O_{39}]^{6-}$, $[W_{12}O_{41}]^{10-}$, etc. From alkaline solution Na_2WO_4 crystallises but when WO_3 is fused with Na_2CO_3 and the mass extracted with water $Na_{10}W_{12}O_{41}.28H_2O$ crystallises.

When more than one acid group is present in the anion of an acid, the acid is callsd a *polyacid.* The polyacids of molybdenum and tungsten are of two types: *isopolyacids* containing only the same kind of acid anions and *heteropolyacids* containing two different kinds of acid anions. Some typical examples are:

Polyacids :	$(NH_4)_2[Mo_7O_{24}]$; $Na_{10}[W_{12}O_{41}]$	
Heteropolyacids :	$H_4[SiO_4(MoO_3)_{12}]$	(12-molybdosilicic acid)
	$H_3[AsO_4(MoO_3)_{12}]$	(12-molybdoarsenic acid)
	$H_5[BO_4(WO_3)_{12}]$	(12-tungstoboric acid)

The yellow precipitate in the molybdate test for phosphate is also a heteropolyacid salt, $(NH_4)_2H[PO_4(MoO_3)_{12}]$. The central element sits at the centre of a tetrahedron, the four corners of which are occupied by four oxygen atoms. Each of these four oxygens at the tetrahedral points are shared by three octahedra of the second acid group (for example Mo of phosphomolybdate). So at the four corners of the central tetrahedron there are twelve MoO_6 octahedra. In the ultimate structure these octahedra are so positioned that they can share corners and edges to give rise to the formula given above. In the 6-acids such as in $(NH_4)_6[MoO_6(MoO_3)_6]$, $M_5[IO_6(MoO_3)_6]$ the central atom is in octahedral surrounding of six oxygen atoms. The surrounding six octahedra of the second acid group share edges in such a way as to create an octahedral hole for the central atom.

Tungsten hexafluoride and molybdenum hexafluoride are made by direct fluorination of the metals. These are covalent and are hydrolysed by water presumably because they can assume a higher coordination number and because they have available empty *d*-orbitals to allow nucleophilic attack.

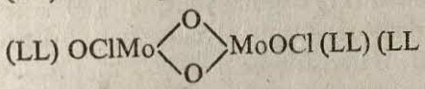
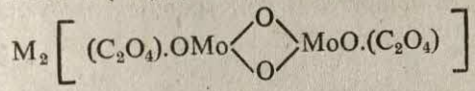
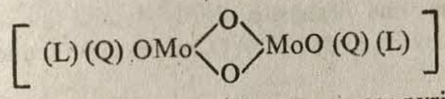
Both molybdenun and tungsten form a large number of oxyhalides. $MoOF_4$ and WOF_4 are obtained by the action of fluorine on MoO_3 and WO_3 respectively. These are colourless, volatile solids. $MoOCl_4$ is obtained as green crystals by refluxing MoO_3 with $SOCl_2$ and evaporating to crystallisation. On heating WO_3 in CCl_4, phosgene or PCl_5 vapour a mixture of $WOCl_4$ and WO_2Cl_2 is formed. The two compounds are separated by making use of their different volatility ($WOCl_4$ being more volatile). $WOCl_4$ forms scarlet crystals and WO_2Cl_2 yellow crystals. MoO_2Cl_2 is made by the interaction of dry MoO_2 and chlorine. It is a colourless solid which sublimes at 250°C.

Since molybdenum (VI) is not an oxidant like chromium (VI) it has been possible to obtain complexes with organic ligands. These are mostly of the dioxo types. $[MoO_2\,(acac)_2]$ is obtained by refluxing MoO_3 with acetylacetone. Yellow coloured $[MoO_2\,(hydroxamate)_2]$ complexes are obtained by the action of aromatic hydroxamic acids (R—CO—NHOH) on molybdates in slightly acid medium. A dimeric oxobridged oxalato complex $K_2[O_2(H_2O)\,(C_2O_4)Mo-O-Mo(C_2O_4)(H_2O)O_2]$ has also been structurally characterised. Similar tungsten complexes have not been sufficiently investigated.

26.3.2. Pentavalent Molybdenum and Tungsten. Molybdenum pentachloride is obtained as dark green crystals by heating powdered molybdenum in chlorine. It is readily hydrolysed by water to $MoOCl_3$ and finally to $MoO(OH)_3$. An acidic (HCl) solution of ammonium molybdate can be reduced by mercury to brown red molybdenyl chloride $MoOCl_3$. This compound can be changed to $MoO(OH)_3$ by boiling with ammonium carbonate. On dissolving $MoO(OH)_3$ in concentrated HCl and on adding NH_4Cl ammonium oxo-pentachloro-molybdate $(NH_4)_2[MoOCl_5]$ can be obtained as brown crystals. The compound is paramagnetic ($4d^1$ system, $\mu \sim 1.7$ B.M.). The oxo-pentachloro-molybdenum (V) species has also been obtained by the reduction of MoO_3 in concentrated HCl by HI and the $[MoOCl_5]^{2-}$ isolated as dipyridyl or o-phenanthroline salt, dipy $H_2{}^{2+}[MoOCl_5]$, o-phen$H_2{}^{2+}[MoOCl_5]$, by the addition of these bases to the reduced solution.

Oxo-pentabromo-molybdenum (V) acid, $H_2[MoOBr_5]$, has been prepared by the reduction of HCl solution of MoO_3 with HBr and then saturating the solution with dry HBr gas. The compound forms green paramagnetic (μ1.67 B.M.) crystals. Salts of this acid have also been isolated.

Recently substantial studies have been reported on complexes of oxo-molybdenum (V). The complexes are of many different types:

1. $MoOCl_3.L_2$ (L = a neutral unidentate donor, eg: $(CH_3)_2SO$)
2. $MoOCl_3.(LL)$ (LL = a neutral bidentate donor, eg: dipyridyl)
3. $(LL)\,MoOCl_2{-}O{-}MoOCl_2(LL)$ (LL = a neutral bidentate eg: dipyridyl)
4. 
$(LL)\,OClMo\langle\overset{O}{\underset{O}{}}\rangle MoOCl\,(LL)$ (LL = a neutural bidentate eg: dipyridyl)
5. $MoOCl\,(AB)_2$ (ABH = a bidentate monobasic acid eg: oxine)
6. 
$M_2\left[(C_2O_4).OMo\langle\overset{O}{\underset{O}{}}\rangle MoO.(C_2O_4)\right]$ (C_2O_4 = oxalate ion)
7. 
$\left[(L)(Q)\,OMo\langle\overset{O}{\underset{O}{}}\rangle MoO\,(Q)\,(L)\right]$ (L = a neutral unidentate donor, eg: pyridine; QH = quinaldinic acid)

These complexes are generally synthesized by the action of the organic ligands on $MoOCl_3$ in alcoholic medium. A typcal set of reactions with quinaldinic acid is shown in Chart 26-I.

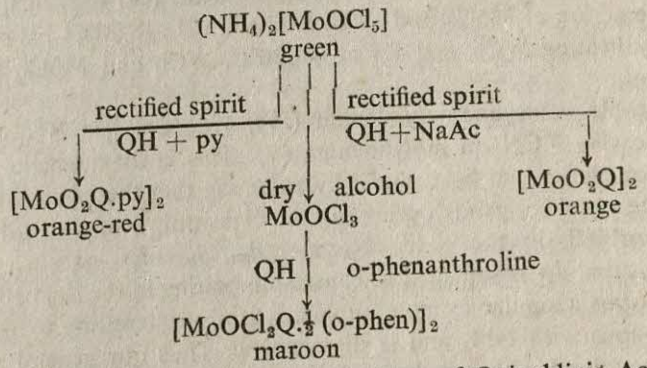


Chart 26–I. Molybdenum (V) complexes of Quinaldinic Acid. (Dutta and Chatterjee, *J. Indian Chem. Soc.* 1967, **44**, 758)

Although oxo-molybdenum (V) complexes should ideally show paramagnetic moment many of the complexes with organic ligands show extremely low moments due to spin-spin interaction of neighbouring molybdenum (V) (cf. oxo-vanadium (IV).

Tungsten pentachloride is obtained as dark green crystal by the reduction of WCl_6 with hydrogen. Both $MoCl_5$ and WCl_5 are monomeric in the vapour state but in crystalline state these are chloro bridged dimers Mo_2Cl_{10} and W_2Cl_{10}. Both $MoCl_5$ and WCl_5 react with $[Et_4N]Cl$ in dichloromethane to give black $[Et_4N]$

$[MoCl_6]$ and green $[Et_4N]$ $[WCl_6]$. Their magnetic moments are lower than the spin-only value. Tungsten analogue of $[MoOCl_5]^{2-}$ is obtained by the electrolytic reduction of WO_4^{2-} in concentrated HCl medium. Blue crystals of $K_2[WOCl_5]$ have thus been isolated. The complexes $M_2[WOBr_5]$ (M = Rb, Cs, NH_4) have been similarly obtained by using HBr. These are coloured brownish yellow. Tungsten (V) complexes on the whole are less stable than those of molybednum (V) and they are also less investigated.

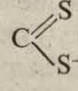
Electronic Spectra: Like oxo-vanadium (IV) oxo-molybdenum (V) is also a d^1 system and is under tetragonal compression. Oxo-molybdenum (V) complexes therefore can exhibit as many as three $d-d$ transitions: $d_{xy} \rightarrow d_{xz}$, d_{yz}; $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{z^2}$. Molybdenum being a member of the second transition series the transition energies will be higher compared to corresponding oxo-vanadium (IV) complexes (cf. Part I, p. 236).

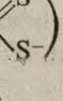
26.3.3. Quadrivalent Molybdenum and Tungsten. Molybdenum dioxide is obtained by the reduction of MoO_2 by H_2 at 450°C. WO_2 can also be reduced to WO_2 by a similar procedure.

$MoCl_4$ (red crystal) is made by heating MoO_2 with CCl_4 in a sealed tube at 250°C or by heating $MoCl_3$ to a red heat in a stream of CO_2. In the latter reaction Mo_6Cl_{12} is formed alongwith $MoCl_4$ which distills over. WCl_4 (black needle) is made by distilling the hexachloride in H_2 at sufficiently high temperature or by reduction of WCl_6 by Al while a temperature gradient of 475°C to 225°C is maintained. Hexachloro molybdenum (IV) complex salts (eg: K_2MoCl_6) are obtained by the interaction of $MoCl_5$ and alkali halide in ICl_5. $K_2[WCl_6]$ is obtained as red crystals by heating WCl_6 and KI at ~ 130°C. WCl_4 and $MoCl_4$ form adducts: eg. $WCl_4.py_2$.

Very stable octacyanomolybdenum (IV), $[Mo(CN)_8]^{4-}$ is obtained by the action of excess KCN on molybdenum (V). This is diamagnetic which can be explained on the crystal field model by assuming that the crystal field set by the eight strong cyanide ligands occupying the eight points of a distorted cube split the five d-orbitals in the order $d_{xy} < d_{z^2} < d_{xz}, d_{yz} < d_{x^2-y^2}$ such that the gap between d_{xy} and d_{z^2} is sufficient to cause spin pairing in the d_{xy} orbital. Tungsten (IV) also forms a similar cyano complex. It is also interesting to note that WCl_4 is isomorphous with NbI_4 and is diamagnetic. Thus our general rule that spin pairing is favoured with members of the second and third transition series holds (Chapter 22).

$Mo(chelate)_2Cl_2$ (chelate = acac, oxin) have been synthesised by treating $MoCl_4(CH_3CN)_2$ with the appropriate ligand in refluxing acetonitrile. These are paramagnetic ($4d^2 : \mu = \sim 2.63$ B.M.).

Complexes $MoOB_2$ (B = diethyldithio carbamate, $(Et)_2$ N =  $C\begin{matrix}^{\nearrow S}\\ _{\searrow S^-}\end{matrix}$

or diethyl dithiophosphate, $(EtO)_2$  $P\begin{matrix}^{\nearrow S}\\ _{\searrow S^-}\end{matrix}$)

have been prepared by (*a*) reducing oxomolybdenum (V) complexes $B_2OMo-O-MoOB_2$ with thiphenol or zinc dust or (*b*) by the reduction with an excess of sodium dithionite of an aqueous solution of sodium molybdate and the appropriate ligand. These complexes are diamagnetic but monomeric. Hence spin pairing by way of oxygen bridge or metal—metal bond is not possible. So these are to be regarded as low spin molybdenum (IV) complexes.

26.3.4. Trivalent Molybdenum and Tungsten. Electrolytic reduction of molybdenum (VI) in concentrated HCl with bright platinum cathode to molybdenum (III) followed by addition of alkali halides gives red coloured $M_3[MoCl_6]$. Similar reduction in presence of NH_4NCS gives $M_3[Mo(NCS)_6]$. Treatment of $K_3[MoCl_6]$ in aqueous ethanolic dipyridyl or o-phenanthroline gives red coloured $[Mo(dipy)_3]^{3+}$ and $[Mo(o\text{-phen})_3]^{3+}$ salts. As expected spin only magnetic moments of such complexes ($4d^3$ system) are $\sim 3.7-3.9$ B.M. It is interesting to note that with lowering of valence the trend of forming oxo-molybdenum complexes has disappeared.

Electrolytic reduction of WO_3 in HCl medium being followed by addition of KCl gives unstable yellow green crystals of $K_3[W_2Cl_9]$. In this compound two tungsten (III) octahedra share a face with three chlorine atoms functioning as bridges. The compound is very nearly diamagnetic. In this compound we note some distinct difference between molybdenum and tungsten.

26.3.5. Bivalent Molybdenum and Tungsten. The so-called dihalides $MoCl_2$ and WCl_2 are really hexanuclear metal atom cluster compounds, $[Mo_6Cl_8]Cl_4$ and $[W_6Cl_8]Cl_4$. '$MoCl_2$' is made by heating the trichloride $MoCl_3$ in a stream of CO_2 when it breaks up into volatile $MoCl_4$ and non-volatile Mo_6Cl_{12}. Metallic molybdenum also reacts with phosgene at 630°C to give Mo_6Cl_{12}. This is a yellow infusible powder. One-third of the halogens is much more easily removed than the rest. Thus on dissolving the compound in HBr or HI, $[Mo_6Cl_8]Br_4$ and $[MoCl_8]I_4$ crystallise. $AgNO_3$ treatment gives $[Mo_6Cl_6](NO_3)_4$. Mild donors can be co-ordinated one each to the six molybdenum, as for example, $[(Mo_6Cl_8)L_6](ClO_4)_4$ ($L = (CH_3)_2SO$). Inside the complex cation the 8 chlorine atoms are at the corners of a cube with the 6 molybdenum atoms slightly above the centres of the 6 faces of the cube.

The tungtsen dichloride should be similar although it has been less elaborately studied.

Reaction of $[MoCl_6]^{2-}$ in ethanolic HCl with o-phenylenebisdimethylarsine (diars) leads to reduction and *trans* $[Mo(diars)_2Cl_2]$ (bright yellow) is obtained. Molybdenum (II) is a $4d^4$ system and inner orbital d^2sp^3 hybridisation leads to two unpaired spins.

Action of different chemical agents on $W(CO)_6$ leads to the following interesting products:

$$W(CO)_6 \xrightarrow{I_2} WI_3 \xrightarrow{\text{diars}} [W(diars)_2I_2] \xrightarrow{CO} [W(CO)_2(diars)I]\,I$$

A molybdenum (II) complex $[Mo(CO)_2(diars)_2I]I$ has also been isolated.

26.3.6. Zerovalent Molybdenum and Tungsten. As expected these low oxidation states are stabilised by π-acid ligands such as CO, diars, PR_3 etc. Both molybdenum and tungsten form hexacarbonyls. These are obtained by the reduction of the halides by phenylmagnesium bromide in the presence of CO. Sodium in diglyme may also be used as the reducing agent:

$$MoCl_5 \xrightarrow[\text{CO}]{\text{Na in diglyme}} Mo(CO)_6;\ WCl_5 \xrightarrow[\text{CO}]{\text{Ph Mg.Br in benzene}} W(CO)_6$$

Both the hexacarbonyls form colourless crystals which can be sublimed in vacuo. These carbonyls undergo partial substitution of the CO groups by other π-acid ligands. Some typical examples are shown with $Mo(CO)_6$:

$$Mo(CO)_6 \xrightarrow[\text{heat}]{\text{pyridine}} [pyMo(CO)_5],\ [py_2Mo(CO)_4],\ [py_3Mo(CO)_3]$$

$$Mo(CO)_6 \xrightarrow{\text{diars}} [(diars)\ Mo(CO)_4]$$

$$Mo(CO)_6 \xrightarrow{\text{toluene}} [(toluene)\ (Mo(CO)_3]$$

26.4. ISOLATION OF THE GROUP VIA ELEMENTS

26.4.1. Chromium. The chief ore of chromium is *chromite* ($FeO.Cr_2O_3$). Chromite is first roasted in air with sodium carbonate and lime:

$$4FeO.Cr_2O_3+8Na_2CO_3+7O_2 \rightarrow 2Fe_2O_3+8Na_2CrO_4+8CO_2$$

The lime helps in keeping the mass porous. The sodium chromate is extracted with water, made acidic with sulphuric acid and treated with KCl when the less soluble $K_2Cr_2O_7$ crystallises. The dichromate is then reduced by heating with NH_4Cl:

$$K_2Cr_2O_7+2NH_4Cl \rightarrow (NH_4)_2Cr_2O_7+2KCl \rightarrow N_2+Cr_2O_3+4H_2O+2KCl$$

The green residue is washed with water to remove KCl and dried. The chromic oxide is mixed with aluminium powder and is placed in a large fireclay crucible placed in large amount of sand. The mixture is then fired by lighting a magnesium ribbon planted into a charge of barium peroxide and magnesium powder. The tremendous heat produced during the reduction results in the fusion of chromium which collects at the bottom. As the reaction is highly exothermic once started it becomes self sustaining:

$$Cr_2O_3+2Al \rightarrow 2Cr+Al_2O_3$$

Reduction of Cr_2O_3 by carbon at ~1400°C and under pressure (to minimise volatilisation of chromium) has also been in use. Chromium obtained by these methods is ~97–99% pure.

Very pure chromium can be obtained by electrolysis of pure potassium chromium alum or of chromic acid. In industrial units ferrochromium is treated with moderately strong H_2SO_4 and nearly boiled. The slurry is treated with water at 80°C and $(NH_4)_2SO_4$ and then filtered to get rid of silica etc. The filtrate is cooled to ~5°C when ferrous ammonium sulphate crystallises out. The mother liquor, on concentration and standing, deposits pure chromium ammonium sulphate. A hot aqueous solution of the alum is fed into the electrolytic cells. The cells are generally lead-lined concrete tanks with stainless steel plates as cathode and silver-lead alloy as anode. The anode compartments are lined with vinyon cloth diaphragms. Optimum pH is 2.1–2.4 and temperature is ~55°C. A diaphragmed cell works better as it does not allow free mixing of the anolyte—where chromic acid is formed—with the catholyte where chromium (III) is reduced to the metallic state via chromium (II). In the absence of NH_4^+ the rate of transference of H^+ through the diaphragm into the catholyte is greater than hydrogen evolution at the cathode. The pH will then fall.

at the anode : $Cr^{3+} \rightarrow Cr^{6+} + 3e;\ 4OH^- \rightarrow O_2 + 2H_2O + 2e$

at the cathode : $Cr^{3+} + e \rightarrow Cr^{2+};\ Cr^{2+} + 2e \rightarrow Cr;\ 2H^+ + 2e \rightarrow H_2$

The brittle chromium deposit is then loosened from the cathode surface by hammering. Note that electrolysis of chrome alum is more economic because twice as much chromium is reduced per coulomb from Cr^{3+} to Cr^0 compared to that from Cr^{6+} to Cr^0.

Ferrochrome is an alloy containing about 65% Cr and 35% Fe. It is obtained by direct reduction of chromite by carbon in an electric furnace:

$$FeO.Cr_2O_3 + 4C \rightarrow 2Cr + Fe + 4CO$$

26.4.2. Molybdenum. The important ores are *molybdenite* (MoS_2) and *wulfenite* ($PbMO_4$). The metal is usually worked up from MoS_2. The ore is concentrated by crushing, grinding and by oil floatation. The concentrated MoS_2 is then roasted in air at 600°C:

$$2MoS_2 + 7O_2 \rightarrow 2MoO_3 + 4SO_2$$

High temperature is avoided during roasting to minimise volatilisation of MoO_3. The trioxide is purified by dissolving in excess ammonia, thus crystallising pure $(NH_4)_2MoO_4$. The pure salt is then decomposed by heating to give pure MoO_3:

$$(NH_4)_2MoO_4 \rightarrow MoO_3 + 2NH_3 + H_2O$$

The metal is finally extracted by aluminothermit process or by reduction with hydrogen at ~1100°C.

26.4.3. Tungsten. The important ores are *wolframite* which is an isomorphous mixture of $FeWO_4$ and $MnWO_4$, and *scheelite* ($CaWO_4$). The concentrated ore is roasted in air with sodium carbonate (or fused with NaOH):

$$4FeWO_4 + 4Na_2CO_3 + O_2 \rightarrow 2Fe_2O_3 + 4CO_2 + 4Na_2WO_4$$

$$2MnWO_4 + 2Na_2CO_3 + O_2 \rightarrow 2MnO_2 + 2CO_2 + 2Na_2WO_4$$

The sodium tungstate is extracted with water and treated with acid. The precipitated tungstic acid is heated to obtain WO_3 which is then reduced by carbon, zinc, aluminium or hydrogen.

26.5. USES OF THE GROUP VIA ELEMENTS

Chromium: This is of great importance in alloy steel. *Nichrome* is an important alloy of nickel (60%), chromium (14%), and iron (15%). It is extensively employed for making the resistance wires of electric furnaces. It is non-oxidisable and has a high melting point. *Stellite* is an alloy of chromium, tungsten and nickel. This is used in the manufacture of high speed tools and cutlery. *Stainless steel* is an alloy of about 64% Fe, 18% Cr and 8% Ni. The high resistance of stainless steels to atmospheric corrosion and to the action of many chemicals accounts for their use in the chemicals-, food- and oil-industries.

Chromium Plating: Usually an electrolyte containing CrO_3 and H_2SO_4 in 100:1 ratio is taken in steel tanks lined with lead alloys or ceramic or plastic material. Lead anodes are best because they are resistant to the electrolyte. Furthermore the small amount of PbO_2 formed on the anode surface can oxidise Cr^{3+} back to hexavalent chromium. Unless Cr^{3+} is oxidised back to CrO_4^{2-} it accumulates and cell resistance becomes too high. The materials to be chromium-plated obviously serve as cathodes. The cathode materials are first cleaned to remove dirt, grease, oxide film, etc. by dipping them in $H_2SO_4-H_2O$ or $HCl-H_2O$ or in alkaline solution. Optimum temperature during electroplating is 25°C.

at the cathode : $Cr^{6+}+3e \rightarrow Cr^{3+}$; $Cr^{3+}+e \rightarrow Cr^{2+}$

$Cr^{2+}+2e \rightarrow Cr$; $2H^{+}+2e \rightarrow H_2$

at the anode : $4OH^{-} \rightarrow O_2+2H_2O+4e$

Molybdenum: Molybdenum increases the hardness and strength of steel at high temperatures, increases the corrosion resistance of Cr—Ni steels and decreases the brittleness of chromium steels. Mo—Cr—Ni steels are known as high speed steels because of their use in high-speed machines. The high temperature developed at the speed at which such tools operate would make ordinary steels lose their hardness.

Tungsten: Tungsten filaments are almost universally used in incandescent lamps. It is used with Ni, V, Mo, Cr, etc. in the production of high speed tools.

26.6. ANALYTICAL REACTIONS OF THE GROUP VIA ELEMENTS

Chromium: This element is included in group IIIA of the qualitative scheme of analysis and is precipitated as $Cr(OH)_3$. This can be readily oxidised to Na_2CrO_4 whence it can be identified as lead or barium chromate or by the peroxychromic acid test. The chromate is acidified and treated with H_2O_2, and the blue peroxychromic acid is extracted into amyl alcohol.

For quantitative determination chromium salts are oxidised by Na_2O_2 and the excess peroxide decomposed by boiling. The solution is then acidified to obtain the dichromate ion. Alternatively chromic compounds can also be oxidised by persulphate ion in the presence of $AgNO_3$ and the excess persulphate decomposed by boiling:

$$2Cr^{3+}+3S_2O_8^{2-}+7H_2O \xrightarrow{(AgNO_3)} Cr_2O_7^{2-}+6HSO_4^-+8H^+$$
$$2S_2O_8^{2-}+2H_2O \longrightarrow O_2+4HSO_4^-$$

The dichromate is then treated with an excess of ferrous ammonium sulphate solution and the excess ferrous is titrated against a standard dichromate solution using a suitable indicator. Instead of using ferrous solution the dichromate solution may be treated with excess KI and the liberated iodine titrated against standard thiosulphate solution using starch as indicator.

Molybdenum: It is precipitated as sulphide alongwith the metals of group II of the qualitative scheme. The MoS_2 precipitate dissolves in yellow ammonium sulphide as $(NH_4)_2[MoS_4]$. An HCl solution of molybdenum (VI) on treatment with NH_4NCS turns blood-red due to the formation of the complex $(NH_4)_3[Mo(NCS)_6]$. The red colour is produced also in the presence of phosphoric acid (difference from iron).

Molybdates are quantitatively estimated as lead molybdate in acetic acid—ammonium acetate medium or as dioxo molybdenum (VI) oxinate, $[MoO_2(oxin)_2]$ at pH 4–7.

Tungsten: On the addition of HCl to a tungstate hydrated tungstic acid is precipitated. The element is a member of group I of the qualitative scheme. On heating, the white precipitate of tungstic acid turns yellow. This may be further confirmed by heating the precipitate with Zn+HCl or with $SnCl_2$ when a blue precipitate is formed.

Tungstates are precipitated as benzidine tungstate from a dilute (0.1*N*) H_2SO_4 solution. The precipitate is ignited to WO_3 and weighed. At pH 7–8 tungstates can be precipitated as $BaWO_4$ and dried at 750°C and weighed.

STUDY QUESTIONS

1. Taking chromium as a typical example discuss the major characteristics of transition elements.

2. Taking chromium as an example show that the chemical properties of an element are functions of its valences.

3. Present a comparative account of the chemistry of molybdenum, tungsten and chromium citing in particular the differences between chromium and the other two elements.

4. Show from the chemistries of vanadium, molybdenum and tungsten that with decrease in oxidation state the tendency of forming oxometal compounds decreases.

5. Write notes on: (*a*) pentavalent molybdenum (*b*) quadrivalent molybdenum and tungsten (*c*) oxidising properties of hexavalent chromium and reducing properties of bivalent chromium (*d*) trivalent molybdenum.

6. Show that spin pairing is favoured with elements of the later transition series.

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27

Group VIIA. Manganese, Technetium and Rhenium

Manganese is widely distributed in nature ranking twelfth in the abundance list. The economically viable ore for extraction of the metal is the *pyrolusite* (MnO_2). Mendeleev had predicted in 1871 that an element of atomic weight around 100 should exist. Moseley laid a sounder basis to Mendeleev's predictions by developing a relation between atomic number of an element and its characteristic X-ray spectrum (Chapter 1). Thus gaps in the Mendeleev Periodic System at atomic numbers 43 (of atomic weight ~100), 61, 72, 75, 85, 87 and 91 were predicted. Search for these 'missing' elements naturally began. Earlier claims of the discovery of the element 43 in naturally occurring ores were discarded as the X-ray lines of the 'new' element and rhenium were almost the same. Radioactivity principles indicate that element 43 should possess no stable isotope. Only chance of finding it lay in some radioactive disintegration product of the neighbouring elements. Perrier and Segre ultimately traced the element among the products of dismutation of a molybdenum target which has been bombarded by deuterons and neutrons. The longest lived isotope of technetium (Tc-99) with a half life (β-decay) of 2.2×10^5 years is now synthesised by slow neutron bombardment of molybdenum-98. The (n, γ) reaction gives molybdenum-99 which decays by beta emission to technetium-99. Rhenium occurs in nature but not as a distinct mineral. Surprisingly it accompanies molybdenum, an element of another group. The relative abundances of the elements in the earth's crust are: Mn (0.1 %) and Re ($\sim 10^{-8}$ %). Fortunately in some Norwegian *molybdenite* ores the rhenium concentration may go upto even 0.001 %, thus making its extraction possible.

27.1. COMPARATIVE STUUY OF THE GROUP VIIA ELEMENTS

27.1.1. General Considerations. This group is composed of the transition elements manganese, technetium and rhenium. The elements possess the outer orbital electronic configurations of d^5s^2. Their properties are typically those of transition elements. They all show variable valences, the upper limit being given by the sum of the *d* and *s* electrons. All possible valences from −1 to +7 have been established in all the three elements. Again in keeping with the general trend observed in the earlier groups the lower oxidation states become less stable with increasing atomic number. Thus with technetium and rhenium the + 7 state is decidedly the stablest and the commonest. With manganese, on the other hand, it is the + 2 state which is the stablest and the + 7 state is observed only in Mn_2O_7 and permanganate. This + 7 state is unstable, being highly oxidising. Many of the various oxidation states occur only in the form of complexes. Because of such a wide array of oxidation states manganese is often hailed as the most versatile element of the first transition series.

Typical of a group of transition elements the ionisation potentials change very little from manganese through technetium to rhenium. Their electronegativities are also low (Table 27.1). The increase from Mn (1.5) to 1.9 (Tc and Re) is due to the values being for + 2 state for Mn and for + 7 state for Tc and Re. The differences between manganese and technetium are rather very wide, and those between technetium and rhenium are only slight. Both technetium and rhenium have similar size (1.36/1.37A) although the atomic weight changes from 99 (Tc) to 186 (Re). This is reflected in the increase of density from 11.5 to 20.5. As in other groups the melting points are high and the change from manganese to technetium and rhenium is very appreciable. Tables 27.1 and 27.2 give the physical properties of the elements.

Table 27.1. Electronic Configurations and Some Properties of Group VIIA Elements

Element	Atomic Number	Electronic Configuration	Ionisation Potential (*ev*)	Electro-negativities
Manganese	25	[Ar] $3d^54s^2$	7.43, 15.64, 33.69 . . .	1.5
Technetium	43	[Kr] $4d^55s^2$	7.28, 15.26 . . .	1.9
Rhenium	75	[Xe] $4f^{14}5d^56s^2$	7.87, 16.6 . . .	1.9

Table 27.2. Some More Properties of Group VIIA Elements

Element	Atomic Radius(A)	Ionic (M^{2+}) Radius(A)	M.P. (°C)	B.P. (°C)	Density (gm/ml)	$E°$ (volts) $M^{2+} + 2e \rightleftharpoons M$
Manganese	1.26	0.80	1245	2097	7.4	−1.18
Technetiun	1.36	—	2150	—	11.5	—
Rhenium	1.37	—	3180	5900	20.5	—

As demanded by the increasing electronegativity, the higher oxides and oxyacids are acidic and the lower ones are basic, Besides, the higher oxidation states give covalent compounds and the lower ones ionic compounds. Thus Mn^{2+} forms a basic oxide and gives ionic compounds whereas the higher oxides are either acidic or amphoteric.

As is the rule with all transition elements, many of the abnormal oxidation states are stabilised through complex formation. Also in keeping with our generalisations (Chapter 10) on the stabilisation of the less familiar oxidation states, higher oxidation states are stabilised by electronegative groups such as F^-, O^{2-} (eg: MnO_4^-, TcO_4^-, ReO_4^-, ReO_3F, etc.). Low oxidation states are stabilised by π-bonding ligands. For example, a very extensive series of air-stable unipositive manganese complexes have been synthesised as hexakis (isocyanide) manganese (I) salts. Carbonyls, carbonylate anions are also known.

Typically also of transition elements, many of the compounds of this group are highly coloured and are often paramagnetic. Thus octahedral manganese (II) in high spin state gives a moment of 5.9 B.M. and in low spin state gives ~1.8 B.M. As expected technetium and rhenium compounds are mostly spin-paired since spin-pairing is favoured due to bigger sized *d*-orbitals and higher nuclear charge.

27.1.2. Chemical Behaviour. *Hydrides:* Very little is known about the hydrides of these elements. There is little doubt, however, that these are of the interstitial type.

Oxides and Oxyacids: The instability of the highest oxidation state with the first member and conversely the greater stability of the highest valence with the heavier elements is shown by the heptoxides. Re_2O_7 can be boiled (350°C) undecomposed while Mn_2O_7 begins to lose oxygen at 0°C. Thus heating a rhenium compound in air produces Re_2O_7 but a manganese compound gives only MnO. $KMnO_4$ starts giving oxygen at 200°C while $KReO_4$ can be distilled unchanged at 1370°C.

In the +7 and +6 states manganese occurs as permanganic acid, $H[MnO_4]$ (violet), and manganic acid, $H_2[MnO_4]$ (green), and their salts. In these two states manganese is acidic and not basic. This behaviour is in conformity with what is found in the preceding groups. Note that the elements of the earlier groups in their highest oxidation state give rise to acids, eg.: H_4TiO_4, H_3VO_4 and H_2CrO_4. Manganese (IV) is also mostly acidic occurring as unstable $(HO)_2MnO$ or H_2MnO_3, However MnX_4 compounds are also known, but these are very unstable. All manganese (IV) compounds readily undergo hydrolysis and precipitate the very insoluble MnO_2. Manganese (II) and (III) are no longer acidic but only basic. Thus manganese (III) forms alums and manganese (II) forms a series of vitriols and schonite type double sulphates.

Halides: Table 27.3 lists the halides and oxyhalides of manganese, technetium and rhenium. Of interest is the absence of any halide, particularly bromide and iodide of manganese, in the higher oxidation states. It is understandable because manganese in the +7, +6 or +5 state would be far too oxidising for the bromide and the iodide ions. Although fluorine is notable for its ability to force highest coordination number it is surprising that no compound like MnF_7 or $MnOF_5$ is known. The higher halides and oxyhalides are on the whole covalent compounds being low melting and low boiling. Some of these can even be distilled in inert atmosphere. The quadrivalent halides, in particular, form halo complexes: K_2ReF_6, M_2ReCl_6, K_2MnF_6 etc. Trivalent manganese fluoride also forms a complex $M[MnF_4]$. As a contrast trivalent rhenium chloride forms metal atom cluster compounds. Thus $ReCl_3$ is really Re_3Cl_9, the trimeric unit is so strong that it persists around 600°C. In presence of excess halide Re_3Cl_9 forms compounds of the type $M_3[Re_3Cl_{12}]$.

Manganese dihalides (pink) are obtained by dissolving the metal in the halogen hydracids. The trihalide MnF_3 is made by the action of fluorine on manganous iodide. MnF_3 reacts with F_2 at 400°C to give blue MnF_4.

The tetrahalides are obtained by the reduction of the higher halides by rhenium at elevated temperature. Rhenium tetrahalides form halo complexes on the reduction of perrhenic acid with halogen hydracids in presence of KI. ReF_6 is obtained by the direct action of fluorine on rhenium at 120°C but at 400°C under pressure ReF_7 is obtained. $ReCl_5$ is obtained as a dark red brown vapour by the action of chlorine on rhenium metal powder at 500°C. The pentachloride on heating in nitrogen decomposes to give the 'trichloride'.

The oxyhalides are generally obtained by the action of halogens on the metal oxides. These are also covalent, low boiling and readily hydrolysed by water.

Table 27.3. Halides and Oxyhalides of Group VIIA Elements

	Oxidation Number					
Element	+7	+6	+5	+4	+3	+2
Manganese	MnO_3F			MnF_4 blue grey solid volatile	MnF_3 red solid	MnF_2 pale $MnCl_2$ pink $MnBr_2$ solid MnI_2
Technetium	TcO_3F yellow, M.P. 18° TcO_3Cl colourless	TcF_6 golden yellow M.P. 33° $TcCl_6$ green	$TcOBr_3$	$TcCl_4$ blood red		
Rhenium	$ReOF_5$ ReO_3F yellow, M.P. 147° ReO_3Cl colourless liquid B.P. 131° ReO_3Br colourless M.P. 39°	ReF_6 yellow M.P.19° $ReCl_6$ green brown M.P. 22° $ReOF_4$ $ReOCl_4$ green brown M.P. 30° $ReOBr_4$, blue decomp. 80°	ReF_5 green yellow M.P. 48° $ReCl_5$ red brown $ReBr_5$ green blue	ReF_4 blue, subl. >300° $ReCl_4$ black $ReBr_4$ red ReI_4 black	Re_3Cl_9 red Re_3Br_9 red brown Re_3I_9 black	

Complexes: The tendency of complexation in manganese is observed distinctly from the +4 state to the lower oxidation states. Nitrogen donor ligands have only recently been induced to form complexes with manganese (+4) and (+3) states. Complexes with oxygen donor ligands such as acetylacetone, oxalic acid, Schiff bases are also known. Unipositive state has been successfully stabilised by isocyanides $C = N-R$ (in$[Mn(CNR)_6]X$), where the metal is bonded to carbon. Zerovalent state is well known in the dinuclear carbonyl, $Mn_2(CO)_{10}$.

Rhenium complexes with the metal in +7 and +6 states are little known. Rhenium (V) complexes are of the oxotype: (*a*) monooxo type eg: $[ReOCl_3(PR_3)_2]$, $[ReOCl_4]^-$ (*b*) trans dioxo type eg: $[ReO_2py_4]^+$, $[ReO_2(en)_2]^+$. Quardrivalent rhenium complexes are well known in rhenioxalates $[Re(OH)_4(C_2O_4)]^{2-}$, in $[ReCl_4(PR_3)_2]$ etc. The phosphine complex is paramagnetic ($3d^3$; $\mu \sim 3.64$ B.M.) as expected but many of the other rhenium complexes give lower magnetic moments. Trivalent rhenium complexes are also known eg: $[Re(diars)_3]Cl_3$, $[(R_3PO)_2ReCl_3]$ etc. Dipositive rhenium has been characterised in several cyano complexes. Zerovalent rhenium is well known in the dimeric carbonyl $Re_2(CO)_{10}$. Monovalent rhenium compounds have also been synthesised eg: $K_5[Re(CN)_6]$.

Technetium has been less studied. On the whole however it resembles rhenium.

27.2. OXIDATION STATES OF MANGANESE

27.2.1. Heptavalent Manganese. Heptavalent manganese is confined to Mn_2O_7, and to permanganic acid and its salts. Permanganic acid and its salts are intense violet, and the heptoxide is green. MnO_4^- is comparable with the perchlorate ion. Manganese in MnO_4^- may be viewed to have a valence shell of $7+1 = 8$ electrons. These 8 electrons may be viewed to be distributed in four pairs in the four tetrahedral d^3s hybrid orbitals of manganese. These make four coordinate links to the four oxygen atoms. Scope of double bonding by the overlap of filled oxygen *p*-orbitals with empty *d*-orbitals of manganese remains. Alternatively manganese in +7 state may be viewed as a $3d^0$ system, the electrons being lost to the oxygens. The counter-cation electron (say from potassium of $KMnO_4$) also goes to the oxygen atoms. Thus all the four oxygen atoms will have filled *p*-orbitals and will be O^{2-} ions which then form four coordinate links to the d^3s hybrid orbitals of manganese. Whichever view we assume permanganate has all paired electrons and hence is diamagnetic. The four manganese–oxygen bond lengths in $KMnO_4$ are the same, namely 1.63A.

Electronic spectra: Heptavalent manganese may be viewed as a $3d^0$ system so that it cannot have any $d-d$ transition. However the high positive charge on the metal may produce ligand-to-metal charge transfer transition i.e. from predominantly ligand $(O^{2-})p$ type M.O.'s to predominantly metal *d*-type M.O.'s (Chapter 10; page 240). The violet colour of $KMnO_4$ ($\lambda_{max} = 545$ nm; $\epsilon = 2253$) belongs to this class.

The Heptoxide: Mn_2O_7 is obtained by adding powdered $KMnO_4$ to concentrated H_2SO_4 when the compound separates as a dark heavy oil. The oil can be purified by slow reduced pressure distillation, and frozen in liquid air to dark green crystals. Around 0°C the compound slowly gives off oxygen and at higher temperature it explodes into MnO_2 and oxygen. With water it gives $HMnO_4$. It is a strong oxidant.

Permanganic Acid and Permanganates: A solution of the acid can be obtained by treating barium permanganate with H_2SO_4. Attempts to isolate the free acid lead to decomposition, precipitating MnO_2 and evolving ozone. Alkali metal permanganates are well known, the solubility of the salts falling with increasing atomic number of the alkali ions.

Potassium permanganate is prepared on a technical scale from pyrolusite, MnO_2. Finely powdered MnO_2 is fused with caustic potash in the presence of air when green potassium manganate is formed:

$$4KOH + 2MnO_2 + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

Potassium manganate is extracted with water and the solution is further oxidised by chlorine or ozone to give the permanganate:

$$2K_2MnO_4 + H_2O + O_3 \rightarrow 2KMnO_4 + 2KOH + O_2$$
$$2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$$

Alternatively the green manganate solution can be oxidised to the permanganate electrolytically. A perforated steel cylinder is used as the cathode. Asbestos cloth or asbestos cement diaphragm is placed over the cathode. Inside this cylinder nickel sheets are suspended to serve as anodes. The manganate solution is charged in the anode compartment of the electrolytic cell. The catholyte is an alkali solution. On electrolysis permanganate crystallises at the anode:

$$MnO_4^{2-} \rightarrow MnO_4^{-} + e$$

According to a modern method an open non-diaphragmed cell is used. The permanganate formed at the anode diffuses to some extent upto the cathode where it is again likely to be reduced to the manganate. This reduction is minimised by employing a cathode of small area. The area of the anode: cathode is in the ratio 10:1. The bath contains $\sim 9\%$ K_2MnO_4 and 5% KOH at 60°C and the applied voltage is 3 volts. A portion of the current is utilised in causing oxygen evolution at the anode ($4OH^- \rightarrow O_2 + 2H_2O + 4e$). The oxidising activity of permanganate is pH dependent:

in acid: $MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{2+} + 4H_2O \; ; E^\circ = 1.51$ volts

in alkali: $MnO_4^- + 2H_2O + 3e \rightleftharpoons MnO_2 + 4OH^- ; E^\circ = 1.23$ volts

in strong alkali: $MnO_4^- + e \rightleftharpoons MnO_4^{2-} \; ; E^\circ = 0.56$ volts

Aqueous solution of permanganates is rather unstable, being sensitive to light. Hence such solutions are stored in amber coloured bottles. Some of the oxidising reactions are shown in the next page.

in acid solution:

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

$$2KMnO_4 + 16HCl \rightarrow 2MnCl_2 + 2KCl + 5Cl_2 + 8H_2O$$

$$2KMnO_4 + 10KI + 8H_2SO_4 \rightarrow 6K_2SO_4 + 2MnSO_4 + 5I_2 + 8H_2O$$

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

$$2KMnO_4 + 5KNO_2 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5KNO_3$$

$$2KMnO_4 + 5SO_2 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

in alkaline solution:

$$2KMnO_4 + H_2O + KI \rightarrow 2MnO_2 + 2KOH + KIO_3$$

$$KMnO_4 + 3NO_2 + 2KOH \rightarrow 3KNO_3 + MnO_2 + H_2O$$

$$2KMnO_4 + 3HCOOK \rightarrow KHCO_3 + 2K_2CO_3 + 2MnO_2 + H_2O$$

$$2KMnO_4 + MnO_2 + 4KOH \rightarrow 3K_2MnO_4 + 2H_2O$$

Although permanganate is a very strong oxidant and although it can serve as its own indicator it cannot be used as a primary standard. It is difficult to obtain the sample in a high state of purity, and completely free from MnO_2. Traces of organic matter in water reacts with $KMnO_4$ to produce MnO_2 which further catalyses the decomposition of permanganate. For analytical purposes permanganate solution is usually standardised against oxalic acid or sodium oxalate. It is commonly used for volumetric estimation of iron, calcium etc., Ferric iron is reduced in HCl medium by $SnCl_2$, excess stannous removed by the addition of $HgCl_2$ (when Hg_2Cl_2 separates), the solution diluted with 2*N* H_2SO_4, Reinhardt solution added and the ferrous titrated by $KMnO_4$. Calcium is precipitated as calcium oxalate which is collected, dissolved in dilute H_2SO_4 and the free oxalic acid titrated against $KMnO_4$. (page 154; Part I).

27.2.2. Hexavalent Manganese. Manganese (VI) is confined to salts of manganic acid (H_2MnO_4). The free acid is unknown and so also the trioxide. Manganates are made by (1) heating manganese dioxide with KNO_3 or (2) by heating MnO_2 with KOH in the presence of air:

$$4KOH + 2MnO_2 + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

$$2KNO_3 + MnO_2 \rightarrow K_2MnO_4 + 2NO_2$$

The manganate is extracted with water and the dark green potassium salt is crystallised. A stable barium salt can also be obtained by adding $KMnO_4$ to a boiling saturated solution of baryta:

$$4Ba(OH)_2 + 4KMnO_4 \rightarrow 4KOH + 4BaMnO_4 + 2H_2O + O_2$$

The manganates are stable in basic solution only. In acid or neutral solution the green colour changes to the purple permanganate with separation of MnO_2:

$$3K_2MnO_4 + 2H_2O \rightarrow 2KMnO_4 + 4KOH + MnO_2$$

$$3K_2MnO_4 + 2H_2SO_4 \rightarrow 2KMnO_4 + MnO_2 + 2K_2SO_4 + 2H_2O$$

The decomposition reaction is certainly promoted by the very small solubility of MnO_2. This is a disproportionation reaction, where a compound undergoes a reaction giving two products—one having a higher valence (in this case managanese (VII) and another a lower valence (manganese (IV)).

Manganates are strong oxidants. Manganates have the same crystal structure as the chromate and the sulphate, and are thus isomorphous with these ions. Manganese (VI) may be viewed as a $3d^1$ system. The magnetic moments of the manganates indicate one unpaired spin.

27.2.3. Pentavalent Manganese. A mixture of MnO_2 and Na_2O_2 react at 500°C with sodium nitrite melt producing an intense blue colouration. Crystallisation of this material from concentrated NaOH solution gives sodium manganate (V) decahydrate $Na_3MnO_4.10H_2O$ as bright blue prisms.

27.2.4. Quadrivalent Manganese. Valence decrease from +7 to +4 has not yet completely changed the acid character of the oxide. MnO_2 shows amphoteric behaviour. As a base it reacts with acids to give salts MnX_4 which with MX forms complexes M_2MnX_6. As an acid it forms with alkalies manganites, M_2MnO_2.

Manganese dioxide is a stronger oxidant in acid medium than in alkaline medium:

$$MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{2+} + 2H_2O \quad ; \quad E^\circ = 1.23 \text{ volts}$$

$$MnO_2 + H_2O + 2e \rightleftharpoons Mn(OH)_2 + 2OH^- \quad ; \quad E^\circ = 0.05 \text{ volts}$$

It reacts readily with hot HCl liberating chlorine

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

With cold concentrated HCl first $MnCl_4$ (dark green) is formed which slowly decomposes to chlorine and $MnCl_2$.

Pure MnO_2 is obtained as lustrous black mass by heating $Mn(NO_3)_2$:

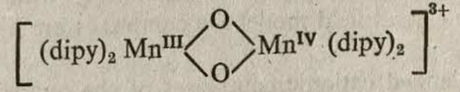
$$Mn(NO_3)_2 \rightarrow MnO_2 + 2NO_2$$

The stability of MnO_2 is mainly due to its insolubility. Careful heating with metal oxides gives manganites which have varying formula, the simplest one being $MnO_2.M^{II}O$ (or $M^{II}MnO_3$). Careful oxidation of $MnSO_4$ in H_2SO_4 with $KMnO_4$ gives black crystals of $Mn(SO_4)_2$ in the cold. The substance is readily hydrolysed in water to MnO_2.

Several complexes are known. The simpler type, for example, the halo complexes $M_2^I[MnX_6]$ (X = Cl, F) are obtained by the reduction of $KMnO_4$ by ether in fuming HCl or HF. Some well established nitrogen donor complexes with biguanide have been reported. These are of the type $[Mn^{IV}(OH)_2(BigH)_2]X_2$. The dark red compounds have been prepared by the following methods: (*a*) by reduction of $KMnO_4$ by ether in the presence of alkaline biguanide and (*b*) by the oxidation of manganous salts with air, H_2O_2 or sodium persulphate in the presence of alkaline biguanide. In alkaline medium the $[Mn(OH)_2(BigH)_2]\,(OH)_2$ is obtained which can be neutralised with appropriate acids to form salts. Although analytical reactions with ferrous ion, and iodide ion definitely establish the +4 state, the magnetic moment of the nitrate salt is low ($\mu \sim$ 2.5 B.M.) for $3d^3$ octahedral manganese (IV). The complex is considered to be magnetically concentrated with interaction between neighbouring manganese (IV) ions. In keeping with this contention the moment value increases in aqueous solution with dilution reaching a value ~ 3.2 B.M.

Negative groups with a central element in a high oxidation state have also been found to stabilise manganese (IV). Alkaline hypochlorite oxidation of manganous chloride in presence of sodium (potassium) paraperiodate $Na_2H_3IO_6$ (or $K_2H_3IO_6$) gives red coloured $Na_7H_4[Mn(IO_6)_3]17H_2O$ (or $K_7H_4[Mn(IO_6)_3]$ $8H_2O$). Oxidimetric, potentiometric and magnetic studies support the +4 oxidation state of manganese. Similar oxidation in presence of sodium (potassium) tellurate gives dark red $Na_7H_7[Mn(TeO_6)_3]3H_2O$ (or $K_6H_8[Mn(TeO_6)_3]5H_2O$ μ = 3.30 B.M.). The periodate and the tellurate ions behave as bidentate (OO) donors (cf: 29-I). Complexes of the type $M_2^I\,[Mn(IO_3)_6]$ have also been synthesised and studied.

An interesting mixed valence complex containing both manganese (IV) and (III) has been described. Thus $[Mn(dipy)_3]^{2+}$ on treatment with $(NH_4)_2S_2O_8$ in acetate buffered medium gives large greenish black crystals of a compound $[Mn(dipy)_2O]_2(S_2O_8)_{1\cdot5}\,3H_2O$. A perchlorate salt $[Mn(dipy)_2O]_2\,(ClO_4)_3$ has been reported. Potentiometric titration against $SnCl_2$ has definitely established the oxidation number of manganese as 3.4—3.5. The following oxo bridged structure has been proposed:



The low magnetic moment (1.73 B.M.) indicates antiferromagnetic interaction.

27.2.5. Trivalent Manganese. With a further lowering of valence all acidic properties have disappeared, and we have an entirely basic element. Mn^{3+} ion exists in solution although disproportionation into MnO_2 and Mn^{2+} ion is facilitated by the insolubility of the MnO_2:

$$Mn_2(SO_4)_3 + 2H_2O \rightarrow MnSO_4 + MnO_2 + 2H_2SO_4$$

That Mn^{3+} exists is verified by the isolation of purple coloured caesium alum $CsMn(SO_4)_2.12H_2O$. A solution of manganous sulphate in 30% H_2SO_4 is taken in a porous pot which is also placed in 30% H_2SO_4 taken in a beaker. Bright platinum foils are used as electrodes. The acidified manganous sulphate solution serves as the anolyte while 30% H_2SO_4 is the catholyte. After a few hours of electrolysis the deep purple anolyte is mixed with a solution of caesium sulphate in 30% H_2SO_4 and the alum crystallised out at ~ 5°C. This is parmagnetic (μ = 4.9

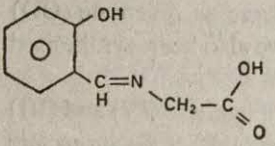
B.M.) which is in good agreement with a high-spin six-coordinate manganese (III) (d^4 ; μ = 4.90 B.M.).

MnF_3 is known as a red solid obtained by the action of fluorine on MnI_2. Halocomplexes of the type M^IMnF_4 and $M_2^IMnF_6$ may be obtained by the addition of metal fluorides to MnF_3. Manganic acetate, a suitable starting material for synthetic studies, is obtained by oxidising manganese (II) acetate in hot glacial acetic acid by chlorine or $KMnO_4$.

Of the organic ligand complexes manganic tris (acetylacetonate) is well known. This forms brilliant greenish black crystals and is obtained by reacting manganic acetate with acetylacetone or by the action of $KMnO_4$ on manganese (II) in the presence of the ligand. The compound is a monomer and is soluble in benzene, ethylacetate, chloroform etc.

$[Mn(acac)_3]$ reacts with biguanide to yield shining red crystals of hydroxo-aquo (biguanide) (acetylacetonato) manganese (III), $[Mn(OH)(H_2O)(Big)(acac)]$. It has an expected moment 4.95 B.M.

Manganous acetate, salicylaldehyde and glycine react in aqueous alcohol under reflux in the presence of sodium/potassium acetate to furinsh dark chocolate red crystals of Na(K) $[Mn(salgly)_2]$ where salgly H_2 represents salicylideneglycine (27-I). The compounds are paramagnetic ($\mu \sim 4.8$ B.M.).



(27-I)

The tris (oxalato) manganate (III) is obtained as deep red-violet crystals by the reaction of $KMnO_4$ with $H_2C_2O_4$ in presence of K_2CO_3:

$$5H_2C_2O_4 + KMnO_4 + K_2CO_3 \rightarrow K_3[Mn(C_2O_4)_3] + 5H_2O + 5CO_2$$

The complex is isomorphous with $K_3[Fe(C_2O_4)_3]$. All these compounds are paramagnetic showing four unpaired spins in conformity with outer orbital sp^3d^2 hybridisation. On the crystal field model the complexes are high spin with $t_{2g}^3e_g^1$ configuration.

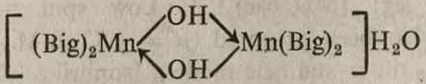
A series of well defined cationic complexes of the quadridentate ethylenedibiguanide, $Et(BigH)_2$ (cf 29-VIII), have been described. The complex base of this series, $[(OH)(H_2O)Mn(Et(Big)_2)]$ has been prepared by the aerial oxidation of a mixture of ethylenedibiguanide sulphate and manganous sulphate in a strongly alkaline medium. The salts, $[(H_2O)_2Mn(Et(BigH)_2)]X_3$ have been isolated from solution of the base in acetic acid by the addition of appropriate salts:

$$\begin{tikzcd}
MnSO_4 + Et(BigH)_2.2H_2SO_4 + NaOH \arrow[d, "air"] & \\
{[(OH)(H_2O)Mn(Et(Big)_2)]} \arrow[r, "H^+"] & {[(H_2O)_2Mn(Et(BigH)_2)]^{3+}} \arrow[d, "X^-"] \\
& {[(H_2O)_2Mn(Et(BigH)_2]X_3}
\end{tikzcd}$$

chocolate red; μ=3.7 B.M.

yellow; μ = 4.8 B.M.

With simple unsubstituted biguanide (BigH) similar aerial oxidation gives insoluble chocolate red crystals of $[(OH)Mn(Big)_2]0.5H_2O$ (vacuum dried) for which a diol bridged structure has been proposed:



$$\left[(Big)_2Mn\begin{matrix}OH \\ OH\end{matrix}Mn(Big)_2\right]H_2O$$

From the filtrate of this preparation some Mn(IV) biguanide complex, described in the previous section, can be recovered.

A low spin (t^4_{2g}) hexacyano complex $K_3[Mn(CN)_6]$ has been obtained by the air oxidation of manganese (II) in excess KCN. Its moment is 2.83 B.M.

It thus appears that biguanide or ethylenedibiguanide is still not strong enough a ligand to force spin-pairing in Mn (III).

Electronic Spectra: A high-spin regular octahedral manganese (III) complex has only one spin allowed but Laporte forbidden transition: $^5E_g \rightarrow {}^5T_{2g}$ (Chapter 11; page 275). But this being a d^4 (t_{2g}^3 e_g^1) system, is under strong Jahn Teller distortion and hence broad or split spectra are often observed. Thus $[Mn(H_2O)_6]^{3+}$ and $[Mn(C_2O_4)_3]^{3-}$ have bands at 21 *kK* and 20 *kK* respectively. Sometimes even three transitions may appear:

$$d_{z^2} \rightarrow d_{x^2-y^2};\ d_{xy} \rightarrow d_{x^2-y^2}; d_{xz},\ d_{yz} \rightarrow d_{x^2-y^2},$$

$[Mn\,(DMSO)_6]^{3+}$ shows three absorption bands at 20,17 and 14.5*kK* (Chapter 10; page 238).

27.2.6. Bivalent Manganese. This is the commonest and the stablest oxidation state of the element. This oxidation state occurs in large number of compounds. Manganous salts are light pink coloured and are obtained by acid treatment of MnO_2. The oxide MnO is a green powder obtained by heating the carbonate in a stream of nitrogen. Addition of alkali to a manganous salt solution precipitates the hyroxide as a white gelatinous solid. This however readily darkens due to its oxidation to MnO_2. The hydroxide is predominantly basic giving salts such as halides, sulphates etc. It reacts slightly with OH^- ion to form $Mn(OH)_3^-$.

Manganous sulphate is commercially obtained by heating pyrolusite with sulphuric acid solution:

$$2MnO_2 + 2H_2SO_4 \rightarrow 2MnSO_4 + 2H_2O + O_2$$

The solution is then treated with insufficient amount of NH_4OH, boiled and filtered to remove the $Fe(OH)_3$ impurity. The filtrate is then crystallised to obtain pure manganous sulphate heptahydrate. Manganous chloride is similarly obtained by the action of HCl on pyrolusite.

Manganese (II) forms complexes but their stability constants are low. Complexes mostly conform to either tetrahedral or octahedral geometry. The tetrahedral tetrahalo complexes $[MnX_4]^{2-}$ can be precipitated from non-aqueous solvents by large cations R_4N^+, R_4P^+, R_4As^+. Some non-electrolytic tetrahedral complexes have also been reported eg: $[Mn(Ph_3PO)_2Br_2]$. These compounds strictly obey the spin only formula showing five unpaired spins (μ = 5.92 B.M.).

Bis (acetylacetonato) manganese (II) is really trimeric, the manganese atoms attaining octahedral stereochemistry through sharing of some oxygen atoms. This complex readily reacts with other donor groups, L, forming monomeric octahedral complexes eg: $[Mn(acac)_2L_2]$. Low spin hexacyano complexes $M_4^I[Mn(CN)_6]$ have also been prepared (μ = 1.73 B.M., one unpaired spin; d^2sp^3 hybridisation; t^5_{2g} on crystal field model). Isonitriles (also called isocyanide) (C = N−R) also produce colourless hexaisocyano complexes $[Mn(CNR)_6]^{2+}$. These are low spin.

Recently manganese (II) complexes of salicylideneglycine (27-I) and related ligands have been synthesised as cream coloured insoluble materials by refluxing manganous acetate with salicylaldehyde and glycine in aqueous ethanol. Since manganese (II) does not provide distinctive moment and spectra, the thermal decomposition curves and the infrared spectra were compared with the dimeric $[Ni(salgly)(H_2O)_2]_2$ and $[Co(salgly)(H_2O)_2]_2$. From these studies the manganese complexes have been identified as dimers, the H_2O molecules occupying trans apical sites and the schiff bases bridging two square planes through their oxygen donor atoms.

Manganese (II) is a $3d^5$ ion and has no *CFSE* in either tetrahedral or in high spin octahedral geometry. A tetrahedral geometry will be preferred to an octahedral one on the ground of minimum ligand-ligand repulsion. It has no preference on crystal field considerations.

Electronic Spectra: $3d^5$ manganese (II) in high-spin state has a $^6A_{1g}$ ground state. All excited states have different multiplicities eg: $^4T_{1g}$, $^4T_{2g}$, $^2A_{2g}$, $^2T_{1g}$ etc. *Thus all electronic transitions of high spin manganese (II) are doubly forbidden i.e. spin multiplicity forbidden as well as Laporte forbidden.* Therefore such transitions are of *extremely low intensity* and are even difficult to identify. This explains why manganous salts are so very pale pink in colour. A typical manganese(II) spectrum is shown in Fig. 27.1. One other interesting feature of the spectrum is the sharpness of some of the bands. One of the factors responsible for broad bands is the changing metal-ligand bond distance. As the ligand atoms vibrate about an equilibrium

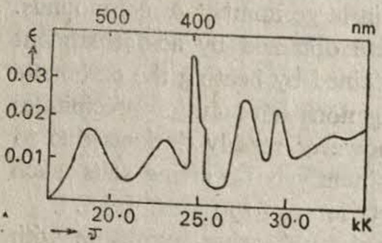


Fig. 27.1. Electronic spectrum of $[Mn(H_2O)_6]^{2+}$

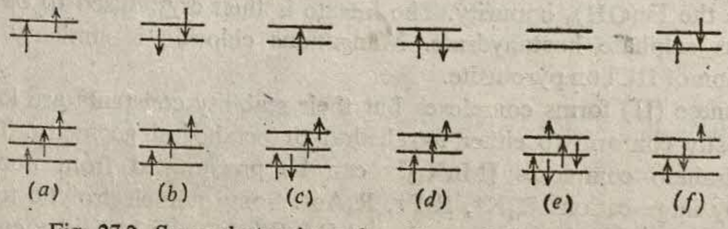


Fig. 27.2. Some electronic configurations of d^5 ion in octahedral field showing different spin multiplicities

position, the crystal field strength, Δ, also changes having a mean value corresponding to the mean position of the ligands. Δ is known to be inversely proportional to the fifth power of the metal-ligand bond length. Therefore those transitions which are functions of Δ ($t_{2g} \rightarrow e_g$) are likely to be broad because these transitions occur over a range of energies as the bonds vibrate. But in high-spin manganese (II) *some transitions* are not of the $t_{2g} \rightarrow e_g$ type (Fig. 27.2). Note that transition from the state (*a*) (Fig. 27.2) to (*b*), (*d*) or (*f*) cannot result from an electron excitation from the t_{2g} level. All the states (*a*, (*b*), (*d*) and (*f*) are $t_{2g}^3\, e_g^2$ but with varying spin multiplicities and electron transitions cannot occur maintaining the same spin multiplicity. Hence a sharp spectrum results in the cases of such transitions. It is also to be noted that excitation of electrons from t_{2g} to e_g results in an excited state with greater metal-ligand distance than in the ground state.

37.2.7. Monovalent Manganese. This less familiar oxidation state has been stabilised in the form of isocyanide complexes. Manganous iodide MnI_2 (anhydrous) reacts with excess of alkyl/aryl isocyaindes to give the following products in alcohol medium:

$$2MnI_2 + 12CNR \rightarrow \underset{\text{colourless}}{[Mn(CNR)_6]I} + \underset{\text{red-brown}}{[Mn(CNR)_6]I_3}$$

The isolation of the two products is based on their different solubilities in alcohol. The colourless iodide salt is more soluble in alcohol than the red brown products. Both the compounds were obtained as crystalline materials.

$[Mn(CNR)_6]I$ behaves as a uni-univalent electrolyte in nitrobenzene, and is diamagnetic. The compound is therefore to be regarded as one of monovalent manganese ($3d^6$; with inner orbital d^2sp^3 hybridisation or t_{2g}^6 on the crystal field model). The other product also behaves as a uni-univalent electrolyte, can be titrated with thiosulphate to $[Mn(CNR)_6]I$, and it is diamagnetic. Addition of iodine to $[Mn(CNR)_6]I$ provides $[Mn(CNR)_6]I_3$. These properties show that $[Mn(CNR)_6]I_3$ is a triiodide salt of $[Mn(CNR)_6]^+$. Thus the above equation is *not* one of disproportionation type:

$$2Mn^{2+} \rightarrow Mn^+ + Mn^{3+}$$

The reduction of Mn^{2+} to Mn^+ is brought about by the excess isocyanide present in the reaction medium. A very large number of substituted isocyanides have been found to stabilise unipositive manganese. The compounds are all air-stable and behave as cations of strong bases. The coordination occurs through carbon and the electron deficient carbon in CNR doubtless assists in the stabilisation of low oxidation state.

The manganese (I) complexes can be oxidised by halogens or fuming nitric acid to blue violet crystalline $[Mn\,(CNR)_6]^{2+}$. These compounds are stable and give moments corresponding to one unpaired electron. Thus these are low-spin $Mn(II)t_{2g}^5$ species.

Action of halogens on $Mn_2(CO)_{10}$ gives $Mn(CO)_5X$ with manganese in the + 1 state. The following series of reactions are also well known:

$$\begin{tikzcd}
Mn_2(CO)_{10} + Cl_2 \arrow[r] & 2Mn(CO)_5Cl \arrow[d, "py"] \\
Mn(CO)_3(py)_2(SCN) & Mn(CO)_3(py)_2Cl \arrow[l, "SCN^-"']
\end{tikzcd}$$

27.2.8. Other Low Oxidation States. Zerovalent manganese is exemplified in the dimeric carbonyl $Mn_2(CO)_{10}$. This is obtained as golden yellow crystals by the action of CO on manganous halides in tetrahydrofuran in presence of a reducing agent. A pressure of ~200 atmospheres of CO and a temperature of ~300°C are necessary. Commonly used reducing agents are Na, Al, Mg or trialkyl aluminium. It melts at 154°C and can be sublimed in vacuo. The structure involves a Mn—Mn bond thus enabling manganese to attain the next noble gas electron number. The Mn—Mn bond can be cleaved in tetrahydrofuran by sodium giving the green carbonylate anion $[Mn(CO)_5]^-$ where manganese is considered to be uninegative.

27.3. TECHNETIUM AND RHENIUM

It has been mentioned in section 27.1 that on the whole chemistries of technitium and rhenium are very similar, and differ widely from that of manganese. The similarity is revealed in their very similar ionisation potentials, very similar electronegativities and very similar atomic radii. The major difference from manganese is shown in their higher oxidation states being more stable than the higher oxidation states of manganese, and the lower oxidation states being unstable compared to those of manganese. Corresponding technetium and rhenium compounds are often isostructural and are of similar reactivities. Manganese generally gives high spin complexes, and low spin complexes are formed by very strong field ligands only. On the contrary technetium and rhenium generally tend to give low spin complexes. For manganese the +2 state is the commonest whereas for technetium and rhenium +7 and +4 states are the commonest and the stablest. Another striking difference with manganese lies in the trivalent halides of rhenium being of the metal cluster type Re_3X_9. Table 27.4 gives some typical compounds of technetium and rhenium.

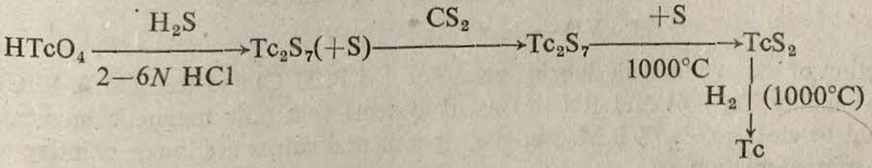
27.3.1. Heptavalent Technetium and Rhenium. This oxidation state is best known in the oxides and oxyacids and their salts. Rhenium heptoxide is the ultimate product of igniting rhenium compounds in oxygen. Re_2O_7 boils undecomposed at 350°C. In water it gives perrhenic acid, $HReO_4$. A large number of salts of this acid are known, and compared to permanganate they are very stable. Thus, whereas $KMnO_4$ starts losing oxygen at 200°C, $KReO_4$ distills unchanged at 1370°C. The perrhenate and the permanganate are both tetrahedral and involve charge transfer type transition from oxide oxygen to the heptavalent metal. This transition in ReO_4^- being at a much higher energy than in MnO_4^-, the former looks colourless.

Table 27.4. Some Compounds of Tc and Re in Different Oxidation States

Oxidation Number	Technetium Compound	Rhenium Compound
+ 7	Tc_2O_7, $MTcO_4$, Tc_2S_7, TcO_3F	Re_2O_7, $MReO_4$, Re_2S_7 ReO_3F
+ 6	TcO_3, TcF_6, $TcCl_6$	ReO_3, ReF_6
+ 5	$TcOBr_3$, $[Tc(diars)_2Cl_4]ClO_4$	R_eCl_5, ReF_5, $ReOF_3$
+ 4	TcO_2, TcS_2, $TcCl_4$, $[Tc(PPh_3)_2Cl_4]$, K_2TeX_6(X = F, Cl, Br, I)	Re_4, $ReCl_4$, ReO_2, K_2ReX_6(X = F, Cl, Br, I)
+ 3	$[Tc(diars)_2Cl_2]Cl$; $[Tc(acac)_3]$ $[Tc(diars)_3]Cl_3$	Re_3Cl_9, $(Ph_3PO)_2ReCl_3$ $[Re(diars)_2]Cl_3$
+ 2	$[Tc(diars)_2Cl_2]$	$[Re(diars)_2Cl_2]$ $M_4[Re(CN)_6]$ $[Re(dipy)_2(CN)_2]$
+ 1	$K_5[Tc(CN)_6]$	$K_5[Re(CN)_6)]$
0	$Tc_2(CO)_{10}$	$Re_2(CO)_{10}$

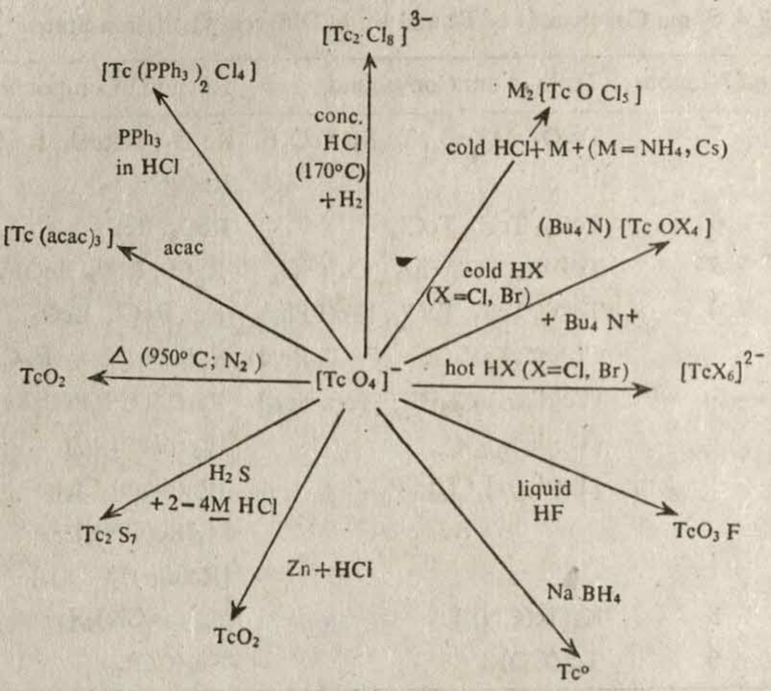
Tc_2O_7 is the product of burning the metal in oxygen at 500°C. The heptoxide is made up of two TcO_4 tetrahedra which share an oxygen atom in a linear Tc—O—Tc array (bridge angle of 180°). The heptoxide dissolves in water to give pertechnetic acid $HTcO_4$ which is known in the form of several salts. Both $HTcO_4$ and $HReO_4$ are strong acids and can be titrated by alkalies in presence of indicators. In general pertechnetates are more soluble than perrhenates. ReO_4^- and TcO_4^- are weaker oxidants than MnO_4^-. For example, in halogen hydracids manganese (VII) is reduced to manganese (II) but rhenium (VII) and technetium (VII) are reduced under similar conditions to the quadrivalent stage. An acid solution of $HTcO_4$ on heating expels volatile Tc_2O_7, a behaviour not shown by rhenium. This difference in behaviour can be utilised in separating the two elements.

The heptasulphides of both elements are obtained by the following scheme (shown for Tc) and these may be reduced to the metal:



$$\begin{tikzcd} HTcO_4 \arrow[r, "H_2S", "2-6N\ HCl"'] & Tc_2S_7(+S) \arrow[r, "CS_2"] & Tc_2S_7 \arrow[r, "+S", "1000^\circ C"'] & TcS_2 \arrow[d, "H_2"', "(1000^\circ C)"] \\ & & & Tc \end{tikzcd}$$

The most striking property of the heptasulphides is their stability. In contrast permanganates will be reduced to manganous ion by H_2S in acid medium and then MnS can be precipitated in ammoniacal medium. In chart 27-I some preparative reactions of pertechnetate are given.



Charr 27–I. Some preparative procedures of technetium compounds beginning with pertechnetate ion.

27.3.2. Hexavalent Technetium and Rhenium. The hexavalent state is exemplifield by the trioxides, salts of technetic and rhenic acids and the hexahalides. ReO_3 is obtained by heating Re_2O_7 with rhenium at 200°C. The tioxide is the anhydride of H_2ReO_4. Alkali perrhenate reacts with ReO_2 on heating in the absence of air to form the green coloured rhenate M_2ReO_4. But these are very unstable in water and decompose to perrhenate and rhenite: $3ReO_3 \rightarrow ReO_2 + Re_2O_7$.

Rhenium metal and chlorine react to give a green vapour which can be condensed to a green brown low melting (M.P.22°C) solid $ReCl_6$. In water it hydrolyses and disproportionates to ReO_4^- and ReO_2. $TcCl_6$ is also obtained as a green volatile compound. But unlike $ReCl_6$, $TcCl_6$ decomposes on heating to $TcCl_4$ and chlorine. $TcCl_6$ hydrolyses, like $ReCl_6$, to TcO_4^- and TcO_2:

$$3Tc(VI) \rightarrow 2Tc(VII) + Tc(IV)$$

Reaction of the metals with fluorine gives TcF_6(M.P. 33°C) and ReF_6(M.P. 19°C).

Assuming Tc(+ 6) and Re(+6) as d^1 systems spin only magnetic moments should be close to ~1.73 B.M. But the experimental values are lower pointing to spin-spin interaction.

27.3.3. Pentavalent Technetium and Rhenium. The pentavalent rhenium is known in several halides ($ReCl_5$, ReF_6), in oxotetrahalo anions ($ReOX_4^-$) and in several oxo- and dioxo-type complexes ($[ReOCl_3.(PPh_3)_2]$; $[ReO_2py_4]Cl$).

Technetium chemistry has not been explored as extensively. This oxidation state is known in technetium compounds like $TcOBr_3$ and $[Tc(diars)_2\,Cl_4]ClO_4$. The latter compound has apparently a coordination number eight.

Rhenium metal powder, contaminated with KCl, reacts with chlorine at ~500°C to give dark red brown vapour of $ReCl_5$ which can be condensed to a solid. Chlorination at a higher temperature gives a mixture of $ReCl_5$ and $ReCl_6$. When heated in an atmosphere of nitrogen $ReCl_5$ breaks up into Re_3Cl_9 and chlorine. When heated with KCl, $ReCl_5$ undergoes a peculiar reaction forming $K_2[ReCl_6]$ and chlorine. This might be an indication of the complexing ability of quadrivalent rhenium. Reduction of ReO_4^- in presence of chloride ion in acidic (H_2SO_4) methanol by zinc gives $[ReOCl_4]^-$ ion. It has a short Re—O bond with the oxygen occupying the apex of a square pyramid. Reduction of ReO_4^- with alkyl phosphines in ethanolic HCl gives $[ReOCl_3.(PR_3)_2]$. The compounds $[ReOCl_4]^-$ and $[ReOCl_3.(PR_3)_2]$ react with pyridine to give $[ReO_2py_4]Cl$. It is interesting to note that although rhenium (V) is a d^2 system all complexes are diamagnetic. Some interesting dipyridyl complexes of rhenium (V) have recently been characterised (Chart 27-II).

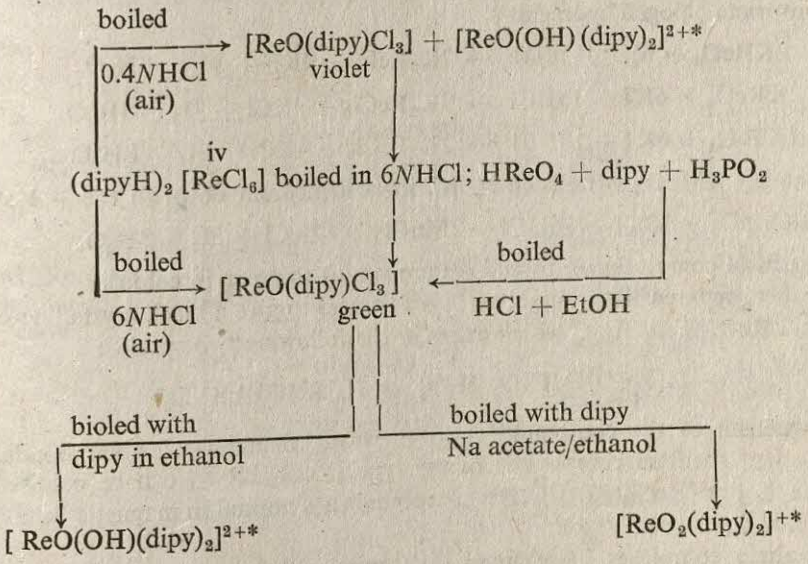


Chart 27-II. Dipyridyl complexes of rhenium (V) (complexes marked with asterisk were isolated as perchlorate salts) (Chakravorti, *J. Inorg. Nucl. Chem*, 1975, **37**, 1991)

Technetium oxytribromide has been obtained by heating TcO_2 in bromine vapour at 350°C. The compound readily undergoes hydrolysis giving +4 and + 7 states:

$$3Tc(V) \rightarrow 2Tc(IV) + Tc(VII)$$

$$3TcOBr_3 + H_2O \rightarrow 2TcBr_4 + HTcO_4 + HBr$$

27.3.4. Quadrivalent Technetium and Rhenium. Outside the + 7 state, + 4 state is the most extensively studied. This state is certainly more stable than manganese (IV). This oxidation state is known in the dioxide, disulphide, tetrahalides, hexahalo complexes and in complexes with organic ligands.

ReO_2 is obtained by heating the metal in a deficient amount of oxygen or by reducing the heptoxide with hydrogen or with the metal at ~ 300°C. A perrhenate solution can also be reduced by zinc and HCl. These comments are valid for TcO_2 as well.

The disulphides of technetium and rhenium are both obtained by the thermal decomposition of the heptasulphides or by the action of H_2S on solutions of quadrivalent metal ions. The disulphides can be oxidised to perrhenic acid/ pertechnetic acid.

Several tetrahalides are known: ReX_4 (X = F, Cl, Br, I) and $TcCl_4$. The higher halides may be reduced by the respective metals. For example ReF_6 can be reduced by Re at ~ 500°C to give ReF_4. Thermal decomposition of the higher halides is also a suitable method eg: $TcCl_6 \rightarrow TcCl_4$. Tetrahalides, in general, are less volatile compared to the hexahalides. Hexahalo complexes are well known. These are obtained by heating potassium perrhenate or pertechnetate with KI in the presence of appropriate halogen hydracids

$$2KReO_4 + 6KI + 16HF \rightarrow 2K_2ReF_6 + 4KF + 3I_2 + 8H_2O$$

$$2KReO_4 + 6KI + 16HCl \rightarrow 2K_2ReCl_6 + 4KCl + 3I_2 + 8H_2O$$

$$2KTcO_4 + 6KI + 16HCl \rightarrow 2K_2TcCl_6 + 4KCl + 3I_2 + 8H_2O$$

Interestingly $KMnO_4$ is reduced by KI in acid medium down to the + 2 state:

$$2KMnO_4 + 10KI + 16HCl \rightarrow 2MnCl_2 + 12KCl + 5I_2 + 8H_2O$$

The hexahalo complexes of Tc and Re are yellow to green in colour.

Freshly prepared ReO_2 dissolves in oxalic acid to give a black crystalline complex acid $ReO.\ C_2O_4.3H_2O$ which exists in the following two species:

$$H[Re(OH)_3.C_2O_4, H_2O] \rightleftharpoons H_2[Re(OH)_4.C_2O_4]$$

Diamagnetism of the compound suggests strong rhenium—rhenium bonds.

Trivalent rhenium compounds of the type $[ReCl_3(PR_3)_3]$ can be oxidised by chlorine to give $[ReCl_4(PR_3)_2]$. The compounds are normal in magnetic behaviour (μ = 3.64 B.M.) for a d^3 ion.

Hexahalo complexes of rhenium (IV) react with heterocyclic bases to give compounds of the type, $[ReX_4.py_2]$.

27.3.5. Trivalent Technetium and Rhenium. Rhenium trichloride, in reality Re_3Cl_9, is obtained by heating $ReCl_5$ in nitrogen when some chlorine is lost and nonvolatile Re_3Cl_9 is left behind as dark red crystals. The freshly made aqueous solution does not give any precipitate with silver salt and so can have no ionisable chloride ion. Previous formulation as halobridged dimer Re_2Cl_6 has been shown by Cotton to be untrue. The real structure consists of Re_3Cl_9 units. The three rhenium atoms are at the points of an equilateral triangle. Each of these rhenium atoms is linked to two chlorine, and there are three chlorine atoms serving as bridges between the rhenium atoms. Re_3Cl_9 cluster can react with neutral donors (L) giving $Re_3Cl_9L_3$, one L being coordinated to one rhenium (III). Monomeric rhenium (III) complexes also exist. Thus reaction of PR_3 or R_3PO with Re_3Cl_9 gives monomeric $ReCl_3(PR_3)_3$ or $ReCl_3(R_3PO)_3$. Reduction of perrhenic acid in the presence of o-phenylenebisdimethylarsine (diars) gives $[Re(diars)_3]Cl_3$ and in the presence of HCl one obtains $[Re(diars)_2Cl_2]Cl$. Complexes of the type $[ReCl(acac)_2(PR_3)]$ are also known.

Reaction of K_2ReCl_6 and dipyridyl (or o-phenanthroline) in a sealed tube gives deep blue violet water-soluble $[Re(dipy)_3]Cl_3$ and $[Re(o\text{-}phen)_3]Cl_3$.

Technetium is less extensively studied. o-Phenylenebisdimethylarsine reacts with pertechnetate to give the complex $[Tc(diars)_2Cl_2]Cl$ and $[Tc(diars)_3]Cl_3$.

27.3.6. Bivalent Technetium and Rhenium. Stannite reduction of $[Tc(diars)_3]Cl_3$ and $[Re(diars)_3]Cl_3$ gives $[Tc(diars)_2Cl_2]$ and $[Re(diars)_2Cl_2]$ respectively. With rhenium sustained studies on cyano complexes have recently been done (Chart 27-III). In contrast to manganese (II) neither rhenium (II) nor technetium (II) forms any tetrahedral complex. Furthermore their complexes are low spin.

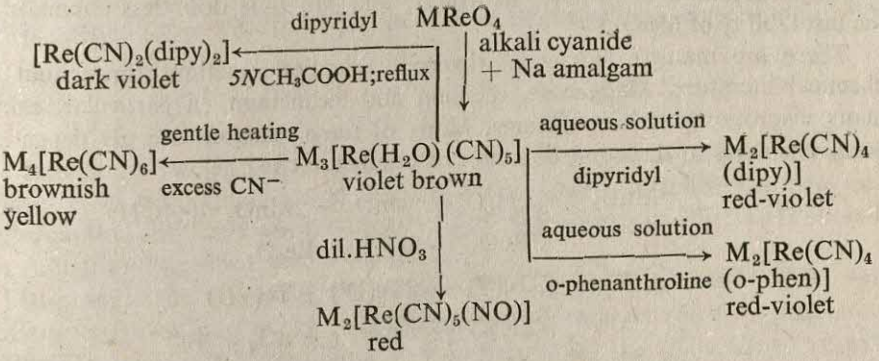


Chart 27-III. Complexes of bivalent rhenium

27.3.7. Other Low Oxidation States of Technetium and Rhenium. As is the general rule these low oxidation states exist in the presence of π-acceptor ligands. Reduction of K_2ReCl_6 in KCN solution by potassium amalgam gives $K_5[Re(CN)_6]$ (green). Similar reduction of TcO_4^- gives $K_5[Tc(CN)_6]$ (olive-green). Both technetium and rhenium form dimeric carbonyls $Tc_2(CO)_{10}$ and $Re_2(CO)_{10}$ with metal-metal bonding. Diamagnetic $Tc_2(CO)_{10}$ has been prepared as colourless solid (m.p. 160°C) by the action of CO (300 atm, 220°C) on Tc_2O_7 for 20 hr. $Tc_2(CO)_{10}$ is isostructural with $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. $Tc_2(CO)_{10}$ and $Re_2(CO)_{10}$ also react with halogens to give $Re(CO)_5X$ and $Tc(CO)_5X$.

27.4. DISPROPORTIONATION (DISMUTATION) REACTIONS

A disproportionation (dismutation) reaction is one where ions in a particular oxidation state break up into an ion of higher oxidation state and an ion of lower oxidation state. In other words a reaction in which a substance oxidises itself and also reduces itself is a disproportionation reaction.

Cuprous ion readily disproportionates into cupric ion and copper (o). The tendency of Cu^+ going over to Cu° is indicated by a potential (E°) value of 0.52 volts. If one Cu^+ is to go over to Cu° another Cu^+ must go to Cu^{2+} so as to make one electron available to Cu^+ for its reduction to Cu°. The tendency of Cu^+ to go over to Cu^{2+} is expressed by the magnitude of its E° being 0.15 volts. Since the driving force of Cu^+ going over to Cu° is much different from the opposing trend of Cu^+ to Cu^{2+}, the Cu^+ ion is able to disproportionate spontaneously. It then follows that an ion will undergo disproportionation when its oxidising and reducing tendencies are appreciable but different. Also when one of these tendencies is appreciable but the other is minimal there will be no spontaneous dismutation.

Disproportionation reactions are also favoured by complex formation as also by precipitation. Thus with ethylenediamine (en) cuprous chloride undergoes disproportionation in aqueous KCl solution.

$$2CuCl + 2en \rightarrow [Cu(en)_2]^{2+} + 2Cl^- + Cu^0$$

Disproportionation of MnO_4^{2-} to MnO_4^- and MnO_2 is doubtless enhanced by the insolubility of MnO_2.

There are many examples of disproportionation reactions throughout the chemical literature. Manganese, rhenium and technetium, in particular, exhibit many disproportionation reactions. Many of these reactions are pH dependent. Some examples of disproportionation reactions are cited below:

$$3MnO_4^{2-} + 2H_2O \rightarrow MnO_2 + 2MnO_4^- + 4OH^-$$

$$3ReO_3 \rightarrow ReO_2 + Re_2O_7$$

$$3Tc(V) \rightarrow 2Tc(IV) + Tc(VII)$$

$$2Mn^{3+} + 2H_2O \rightarrow Mn^{2+} + MnO_2 + 4H^+$$

$$2Cu^+ \rightarrow Cu + Cu^{2+}$$

$$3In^+ \rightarrow 2In + In^{3+};$$

$$2U(V) \rightarrow U(VI) + U(IV)$$

27.5. ISOLATION OF THE ELEMENTS

27.5.1. Manganese. This is present in nature mostly as *pyrolusite* (MnO_2). Other less important sources are: *braunite* (Mn_2O_3), *manganite* ($Mn_2O_3.H_2O$) and *hausmannite* (Mn_3O_4). The common method of extraction involves reduction of the pyrolusite with aluminium powder (aluminothermit process):

$$3MnO_2 + 4Al \rightarrow 3Mn + 2Al_2O_3$$

This reaction may become violent. In order to counter the violent reaction, MnO_2 is heated to redness to form Mn_3O_4 which is then reduced by aluminium:

$$3MnO_2 \rightarrow Mn_3O_4 + O_2; 3Mn_3O_4 + 8Al \rightarrow 9Mn + 4Al_2O_3$$

Pyrolusite can also be worked with acids to give manganous salts and the manganous salts then electrolytically reduced to yield pure manganese. Electrolysis is however not an easy affair with manganese. The metal being quite electropositive readily dissolves in acid solution so that the cathode area must not contain any acidic electrolyte. On the other hand alkaline solution precipitates manganese oxides. A compromise is made by using a diaphragmed cell, the anolyte being a solution of $MnSO_4$, $(NH_4)_2SO_4$ and H_2SO_4 at pH 1 while the catholyte contains $MnSO_4$, $(NH_4)_2SO_4$ and little SO_2 at pH 7.2–7.6. Cells are made of concrete lined with lead. Silver lead alloy plates serve as anodes, stainless steel plates as cathode and cotton canvas as the diaphragm. Reasonably pure $MnSO_4$ is used so as to achieve as high a purity as 99.9% in electrodeposited manganese. Manganese deposits are removed from the cathode sheets as chips by hammering.

27.5.2. Technetium. Technetium has several isotopes of which technetium-99 is the most important. The interaction of molybdenum-98 with slow neutrons yields molybdenum-99 by (n, γ) process:

$${}^{98}_{42}\text{Mo} + {}^{1}_{0}n \rightarrow {}^{99}_{42}\text{Mo} + \gamma$$

Molybdenum-99 then decays with a half life of 69 hours to form technetium*-99:

$${}^{99}_{42}\text{Mo} \rightarrow {}^{99}_{43}\text{Tc}^{*} + {}^{0}_{-1}e\,;\quad {}^{99}_{43}\text{Tc}^{*} \xrightarrow[6\text{ hr}]{\gamma} {}^{99}_{43}\text{Tc}$$

This technetium*-99 undergoes an isomeric transition (γ-emission) and produces technetium-99 with a half life of 2.2×10^5 years. Uranium fission has provided good quantities of Tc-99 via the decay of the fission product Mo-99. Tc-99 is a beta emitter and produces stable Ru-99.

The uranium fission wastes are treated with acid and excess $HClO_4$. To this solution a large cation salt, tetraphenylarsonium chloride, is added to precipitate $[As(Ph)_4]TcO_4$. This is then dissolved in concentrated H_2SO_4 and electrolysed. The precipitated TcO_2 is oxidised to Tc_2O_7 by $HClO_4$, and Tc_2O_7 is then distilled out of solution. The oxide is next reduced to the metal with hydrogen. Alternatively the $[As\ (Ph)_4]\ TcO_4$ is dissolved in alcohol and passed through an anion exchange resin in the chloride form. $[As(Ph)_4]Cl$ passes out of the column and TcO_4^- is retained. The pertechnetate ion is then eluted from the column by $2N\ HClO_4$ and is purified by distillation as Tc_2O_7.

It is worthwhile to narrate the identification of technetium as the element 43 belonging to group VII alongwith manganese and rhenium. The molybdenum–neutron bombardment product was dissolved in aqua regia and the solution was evaporated to dryness. Little manganese and rhenium salts were added and the material dissolved in water and the metals precipitated as sulphide. The sulphide precipitate was then treated with dilute HCl whereby MnS passed into solution but Re_2S_7 remained insoluble. The radioactivity due to technetium was found entirely in the Re_2S_7 residue. The sulphides were then converted to perrhenate and pertechnetate, which were fractionally crystallised.

27.5.3. **Rhenium.** Its major source is *molybdenite* (MoS_2) where it is present as a minor constituent. Rhenium is recovered on a substantial scale from the flue dusts in the roasting of molybdenite ore. Extraction of the flue dust by water gives molybdate and perrhenate. The solution is concentrated and perrhenate precipitated as $KReO_4$ by the addition of KCl. The product at this stage is a grey mass which is next dissolved in hot dilute NaOH. Some hydroxides of other contaminant elements precipitate out. Cooling of the filtrate leads to crystallisation of $KReO_4$. Re_2S_7 can also be precipitated from the ReO_4^- solution by H_2S. The perrhenate or the heptasulphide can be reduced to metallic rhenium with hydrogen.

27.6. USES OF THE GROUP VIIA ELEMENTS

Manganese: In steel industry alloys containing manganese and iron are in great demand. Alloys with 70-80% manganese are known as *ferromanganese*, and those with 15-20% manganese are called *spiegeleisen*. These are obtained by reducing a suitable mixture of iron and manganese oxides with carbon in a blast furnace. The alloys thus obtained contain some carbon. Manganese is an excellent scavenger in steel industry, and improves the quality of steel by removing traces of oxygen and sulphur in the form of oxides and sulphides which are carried away in the slag. Incorporation of manganese in alloy steel is done via addition of ferromanganese or spiegeleisen. Alloy steels containing 8-10% manganese are very hard and resistant to wear and abrasion. These steels are used in rails, rock crushers, conveyor chains and in other tough machineries. Among the more important non-ferrous alloys of manganese are the *manganese bronzes* (Cu, 55-65%; Mn 16-17%; zinc 20-30%). These contain little iron (0.5-2%). Note that these alloys are called bronzes although they do not have any tin. *Manganin* consists of 84% Cu, 12% Mn, 4% Ni and traces of iron. The electrical resistance of manganin changes but little with temperature and hence this alloy is used in the manufacture of standard resistance for electrical equipments.

Rhenium: Rhenium-tungsten thermocouple is serviceable upto ~ 2000°C. It has been found useful as a catalyst in dehydrogenation of a number of alcohols to aldehydes and ketones. A 90% W−10% Re catalyst has also been patented for conversion of SO_2 to SO_3.

Technetium: ${}^{99}_{43}Tc^*$ is a useful γ ray emitter. The nuclear properties of this isotope are ideal for diagnostic nuclear medicine ($t_{\frac{1}{2}} = 6$ hr). Several oxidation states of technetium show varied chemistry and hence ${}^{99}_{43}Tc^*$ can be included in various formulations which are specific for different organs like kidneys, brain, liver, lungs, bones, etc.

27.7. ANALYTICAL REACTIONS OF MANGANESE AND RHENIUM

Manganese: This appears in group IIIB of the qualitative scheme of analysis. In NH_4Cl-NH_4OH medium manganese is precipitated as MnS and is finally tested as the violet permanganic acid. For this purpose manganese is oxidised in HNO_3 solution by sodium bismuthate.

$$2Mn(NO_3)_2 + 5NaBiO_3 + 16HNO_3 \rightarrow 2HMnO_4 + 5Bi(NO_3)_3 + 5NaNO_3 + 7H_2O$$

For quantitative estimation bismuthate oxidation is done in presence of nitric acid in the cold and the solution filtered. The filtrate is treated with an excess of standard ferrous ammonium sulphate and the excess ferrous titrated with a standard 0.03*N* $KMnO_4$ solution. Instead of bismuthate, peroxysulphate oxidation may also be done in presence of silver nitrate catalyst in dil. $H_2SO_4-H_3PO_4$ medium.

$$2Mn^{2+} + 5S_2O_8{}^{2-} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

The excess peroxysulphate is decomposed by boiling and the permanganate titrated as above. Gravimetrically manganese may be precipitated as $MnNH_4PO_4.H_2O$ in slightly ammoniacal solution containing excess of ammonium salts. The precipitate may be ignited to $Mn_2P_2O_7$°.

Rhenium: All rhenium compounds are to be decomposed and rhenium oxidised to ReO_4^- by ammoniacal H_2O_2. The perrhenate is then precipitated with *nitron* as nitron perrhenate and weighed.

STUDY QUEST[ONS

1. "Manganese is a versatile transition metal." Justify from a study of its chemistry.
2. "Technetium chemistry is far closer to rhenium than to manganese." Elucidate.
3. Present a resume of the different oxidation states of manganese.
4. Write an essay on potassium permanganate dealing with its synthesis, oxidising power and analytical uses.
5. Write notes on: (*a*) quadrivalent manganese (*b*) quadrivalent rhenium (*c*) dismutation reaction (*d*) univalent manganese.
6. Discuss the π-acid complexes of manganese.
7. Present a critical appreciation of the electronic spectra of high spin manganese (II) complexes. Do you think that the electronic spectra and magnetic moments of high spin manganese (II) complexes are of any value in identifying the octahedral and tetrahedral stereochemistries?
8. From the nature of the electronic spectra of potassium permanganate explain why this serves as its own indicator in redox titration.
9. Both potassium permanganate and potassium dichromate give charge transfer transitions with high molar absorbance. Yet permanganate serves as self indicator while dichromate cannot. What explanation would you offer?

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28

Group VIII. Iron, Cobalt, Nickel and the Platinum Metals

28.1. INTRODUCTION

This is the biggest group in the Periodic Table and contains the three triads. Fe, Co, Ni; Ru, Rh, Pd; and Os, Ir, Pt. All these elements are transition metals and give rise to all characteristic properties: variable valence, coloured compounds, paramagnetism and complexes. Their closeness in properties led Mendeleev to assign to each triad a single position in group VIII. Since Mendeleev's proposal much studies on the chemistry of these elements have been made. These studies revealed that there is much more of a vertical relationship among the different triads than a horizontal relationship in a particular triad. For example cobalt chemistry is far closer to the chemistries of rhodium and iridium than to those of iron and nickel. Therefore the true division in group VIII should be as: VIIIA containing Fe, Ru and Os; VIIIB containing Co, Rh and Ir, and VIIIC consisting of Ni, Pd and Pt. We enumerate some general characteristics of this group as a a whole.

The electronic configurations of these elements are not known with certainty in the cases of the heavier members. The following outer orbital configurations are believed to be the closest to reality:

Fe $3d^6 4s^2$	Co $3d^7 4s^2$	Ni $3d^8 4s^2$
Ru $4d^7 5s^1$	Rh $4d^8 5s^1$	Pd $4d^{10}$
Os $5d^6 6s^2$	Ir $5d^7 6s^2$	Pt $5d^9 6s^1$

The first ionisation potential virtually remains stagnant for Fe(7.9 *ev*), Co(7.86), Ni(7.63), Ru(7.56) and Rh(7.46) and then slowly increases to Pt (9.0). We have noted for earlier transition groups that there is almost a two-fold increase in density from the second member of a group to the third. This also holds for this group. Note the density (gm/ml) data. Fe(7.9), Ru(12.2), Os(22.5); Co(8.7), Rh(12.4), Ir(22.4); Ni(8.9), Pd(11.9), Pt(21.4). Although atomic number substantially increases from a member of the first triad to the corresponding members of the second and the third triad due to lanthanide type contraction there is hardly any increase in the atomic and ionic radii. This is reflected in the density of the metals and in a strong complexing tendency of the members of the later triads. Indeed we rarely find aquated ions for the second and the third triads.

Typical of all transition elements they all exhibit numerous oxidation states. For example iron can assume valences 6, 4, 3, 2, 1, 0,—2; cobalt can show valences 3, 2, 1, 0,−1 and nickel 4, 3, 2, 1, 0. Members of the later triads can show higher valences of 8, 6, etc. If we consider the *s* electrons of these elements back into the *d* levels the electronic configurations of the atoms become d^8, d^9 and d^{10}. With so many filled *d*-orbitals the elements are expected to form π-acid complexes with ease. In fact they do.

The second and the third triads frequently occur in nature together and they have many properties in common. These six elements are therefore known as the family of platinum metals. Relative abundances of the elements are: Fe(5.0%); Co(0.004%), Ni (0.008%) ; platinum metals (2×10^{-5}%). We now discuss the chemistry of the first triad taken together. It will be followed by a discussion of the chemistry of palladium and platinum.

28.2. COMPARATIVE STUDY OF THE IRON TRIAD

28.2.1. General Considerations. All the three elements iron, cobalt and nickel have incomplete *d*-subshells in their atoms and ions. They are therefore transition elements and in fact much of our knowledge of transition metal chemistry has originated from studies of this triad. The electronic configurations for these elements are two electrons on the 4*s* orbital and six, seven and eight in the 3*d* orbitals for iron, cobalt and nickel respectively (Table 28.1).

It will be recalled that ionisation potentials in a series of transition elements vary but little with increasing atomic number. This is evident from the first ionisation potentials: Fe(7.9 *ev*), Co(7.86) and Ni(7.63). The standard potentials for the couples M^{2+}/M are all negative but indicate a decreasing electropositive character from iron to cobalt and to nickel. Electronegativities of the three elements remain the same. Atomic radii and to some approximation the ionic radii also remain the same. All the elements possess high melting points and boiling points and all have a high density.

Table 28.1. Electronic Configurations and Some Properties of the Iron Triad

Element	Atomic Number	Electronic Configuration	Ionisation Potential (*ev*)	Electro-negativity
Iron	26	$[Ar]3d^64s^2$	7.90	1.8
Cobalt	27	$[Ar]3d^74s^2$	7.86	1.8
Nickel	28	$[Ar]3d^84s^2$	7.63	1.8

Table 28.2. Some More Properties of the Iron Triad

Element	Atomic Radius (A)	Ionic (M^{2+}) Radius (A)	M.P. (°C)	B.P. (°C)	Density (gm/ml)	E° (volts) $M^{2+} + 2e \rightleftharpoons M$
Iron	1.26	0.76	1535	2735	7.9	−0.44
Cobalt	1.26	0.74	1480	3550	8.7	−0.277
Nickel	1.25	0.69	1455	2732	8.9	−0.25

In the first transition series upto manganese we have observed that the highest oxidation state is given by the sum of all the 4*s* and 3*d* electrons. Such consideration should have led to +8, +9 and +10 as the highest oxidation states for iron, cobalt and nickel respectively. But in practice we observe no more than +6 in this triad, this being shown by iron alone. However, a number of oxidation states are observed:

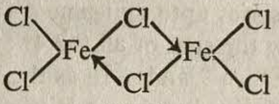
Iron	+6	+4	**+3**	*+2*	+1	0	...	−2
Cobalt	...		+3	**+2**	+1	0	−1	...
Nickel	...	+4	+3	**+2**	+1	0	...	...

Hexavalent iron is very unstable and is observed in only one kind of compounds (*ferrates*, FeO_4^{2-}). For iron, +3 state is the commonest and the next best known state is +2. For cobalt the +3 state is known in innumerable number of complexes but rarely in simple compounds. The +2 state is the commonest for cobalt and is known in complexes and in simple compounds. For nickel the commonest state is +2.

28.2.2. Chemical Behaviour. *Hydrides:* All these elements being transition type their hydrides belong to the group of interstitial hydrides. These are of uncertain composition.

Hydroxides: Acid character of a metal oxide or a hydroxide increases with increasing electronegativity of the metal, which again increases with increasing oxidation state of the metal (Chapter 8). Thus iron (+6) is entirely acidic, the hypothetical oxide FeO_3 being stabilised in the form of *ferrate* ion in alkaline medium. The iron (+3) oxide, commonly written as $Fe(OH)_3$, is better represented as hydrated oxide $Fe_2O_3.nH_2O$. It is readily soluble in acids to give iron (III) salts but is also slightly soluble in strong bases. With alkali metal hydroxides *ferrites* (M^1FeO_2) can be obtained. Ferrous hydroxide when prepared in an oxygen-free atmosphere is white. This is mostly basic and certainly more basic than ferric hydroxide but still possesses some weak acid character. Thus in boiling 50% NaOH ferrous hydroxide gives $Na_4[Fe(OH)_6]$. The cobalt (II) hydroxide is mainly basic dissolving in acids to produce cobalt (II) salts. However in very concentrated alkali a blue solution is obtained, from which $Na_2[Co(OH)_4]$ can be crystallised. The voluminous precipitate of $Ni(OH)_2$ is also readily soluble in acids to gives nickel (II) salts. This hydroxide appears to be basic only, since no nickelate (II) of any type has so far been reported. The nickel (IV) and nickel (III) oxides appear to be predominantly acidic since the few compounds of nickel that are known in these oxidation states have been stabilised only in alkaline medium.

Halides: With iron (III), FeF_3, $FeCl_3$ and $FeBr_3$ have been obtained by the action of excess halogens on iron. FeI_3 is not known due to the strong reducing property of the iodide ion : $Fe^{3+} + I^- \rightarrow Fe^{2+} + \frac{1}{2}I_2$. Of these $FeCl_3$ is best studied. In the vapour phase and in organic solvents it is a dimer (28-I). Dimerisation evidently gives a more stable four coordinate stereochemistry compared to the rather unusual three coordinate geometry.



(28-I)

The anhydrous halides are apparently covalent. $FeCl_3$ crystallises from water as the hexahydrate, in which the $[Fe(H_2O)_6]^{3+}$ exists. CoF_3 is known and is obtained by passing fluorine over $CoCl_2$ at 150°C. This is the only paramagnetic species of cobalt (III). Nickel (III) does not form any simple compound. Dihalides of all these three elements are known. The iron (II) dihalides are obtained by the action of the halogens in the presence of excess metal or by the action of dry HX on the heated metal. Similar methods are also applicable to the other metal dihalides. All the metals react with aqueous HX to form the hydrated halides. Ferrous halides $FeCl_2.6H_2O$ (pale green), $FeBr_2.6H_2O$ (pale green) and $FeI_2.6H_2O$ (pale green) possess *trans* dihalo tetraaquo octahedral structures in the solid state. These assume the hexaaquo structure in aqueous solution. Cobalt (II) halides form hexahydrates, and possess hexaaquo octahedral structures. Nickel (II) halides are also hexahydrates, structural studies showing, like iron (II), *trans* dihalo tetraaquo species in the solid state.

Vitriols, Schonites and Alums: All the three elements form vitriol type sulphates $M^{II}SO_4.7H_2O$. Structural studies show the cations to be six coordinated with aqua groups, the seventh one being hydrogen bonded to the sulphate ion. These vitriols are isomorphous with each other and form mixed crystals. All the three sulphates also form schönite type double sulphate $M_2^ISO_4.M^{II}SO_4.6H_2O$. Of these Mohr's salt $(NH_4)_2SO_4.FeSO_4.6H_2O$ is often used in analytical work. The schonites are also isomorphous with each other. Since iron (III) and cobalt (III) (but not nickel (III)) are known as aquo ions alum type double sulphates are obtained: $M^IFe(SO_4)_2.12H_2O$ and $M^ICo(SO_4)_2.12H_2O$.

Complexes: Taking the two common oxidation states +2 and +3 we have the following d^n ions:

iron	(+2) $3d^6$	cobalt	(+2) $3d^7$	nickel	(+2) $3d^8$
iron	(+3) $3d^5$	cobalt	(+3) $3d^6$	nickel	(+3) $3d^7$

It may be recalled (Chapter 10) that in the octahedral crystal field model $3d^4$, $3d^5$, $3d^6$ and $3d^7$ ions are capable of exhibiting a high spin state and a low spin state depending on the strength of the crystal field, that is, on the complexing ability of the ligands. We have also seen that a weak crystal field induces a tetrahedral stereochemistry. We therefore have the following general behaviour of the triad:

1. Very weak ligands such as those at the extreme left hand region of the spectrochemical series will induce a tetrahedral field. Thus the halo complexes of iron, cobalt and nickel $[FeX_4]^-$, $[CoX_4]^{2-}$ and $[NiX_4]^{2-}$ are all tetrahedral. No extra spin pairing is forced by these ligands. Thus $[FeX_4]^-$ has 5 unpaired spins ($e^2t_2^3$; $\mu = 5.9$ B.M.),, $[CoX_4]^{2-}$ has 3 unpaired spins ($e^4t_2^3$; $\mu > 4.5$ B.M.) and $[NiX_4]^{2-}$ has 2 unpaired electrons ($e^4t_2^4$; $\mu > 3.5$ B.M.).

2. With ligands stronger than the halide ions octahedral stereochemistry with high spin state will be induced. This happens with ligands like H_2O, NH_3 etc. Thus $[Fe(NH_3)_6]^{3+}$ is high spin ($t^3_{2g}e_g^2$; $\mu \sim 5.9$ B.M.) and so also are $[Ni(H_2O)_6]^{2+}$ ($t_{2g}^6e_g^2$; $\mu \sim 3.0$ B.M.) and $[Co(H_2O)_6]^{2+}$ ($t^5_{2g}e_g^2$; $\mu > 4.7$ B.M.).

3. With the strongest ligands the low spin form is favoured since 10 Dq now is larger than the pairing energy of the electrons. This happens with ligands like cyanide, o-phenanthroline, dipyridyl, etc. Thus $K_3[Fe(CN)_6]$ is low spin (t_{2g}^5, 1.9 B.M.) as also are the diamagnetic $K_4[Fe(CN)_6]$ (t_{2g}^6), $[Fe(dipy)_3]^{2+}$ (t_{2g}^6) and $K_3[Co(CN)_6]$(t_{2g}^6).

4. A special mention of the $3d^6$ cobalt (III) needs to be made. In the low spin state (t_{2g}^6) cobalt (III) has a very high crystal field stabilisation energy. Recall (Chapter 10) each t_{2g} electron has a stabilisation energy of $-4\ Dq$. The difference in energies of the high spin state and the low spin state is the highest for cobalt (III) and hence spin pairing is a common feature of all cobalt (III) complexes. The only exceptional case is that of $K_3[CoF_6]$ which is high spin ($t_{2g}^4e_g^2$; $\mu > 4.9$ B.M.).

The reader should check that we will arrive at the above results also from Pauling's hybridisation model (Valence Bond Theory). According to the V. B. theory very weak ligands generate only the high spin tetrahedral sp^3 complexes. In octahedral geometry weak ligands give outer orbital high spin sp^3d^2 and the strong ligands the inner orbital low spin d^2sp^3 complexes.

The octahedral stereochemistry changes, on pulling two *trans* ligands apart, to a square planar geometry (tetragonal distortion). The five *d*-orbitals are then ordered as in Fig. 10.15. If the separation between the two highest energy *d*-orbitals ($d_{x^2-y^2}$ and d_{xy}) is large spin pairing will be forced for d^8 nickel (II). Thus square planar nickel (II) complexes such as $[Ni(DMG)_2]$, $[Ni(BigH)_2]X_2$ have the configuration d^2_{xz}, d^2_{yz}, $d^2_{z^2}$, d^2_{xy}. $3d^7$ cobalt (II) square planar complexes will have one electron in the d_{xy} orbital. On valence bond model we have to use the dsp^2 hybridisation.

28.3. OXIDATION STATES OF IRON

28.3.1. Hexavalent Iron. This oxidation state of iron is met only in the ferrate FeO_4^{2-}. This is obtained as an intense purple solution on oxidation of ferric hydroxide by chlorine in strongly alkaline medium:

$$2NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O$$

$$2Fe(OH)_3 + 3NaOCl + 4NaOH \rightarrow 2Na_2FeO_4 + 3NaCl + 5H_2O$$

When a saturated solution of Na_2FeO_4 is dropped on solid KOH the comparatively less soluble K_2FeO_4 crystallises as an intense red-black product. The carmine red $BaFeO_4$ separates on the addition of barium chloride to an aqueous solution of K_2FeO_4. Electrolytic oxidation of an alkali suspension of $Fe(OH)_3$ also gives a solution of FeO_4^{2-}.

Potassium ferrate is an extremely strong oxidant, being stronger than $KMnO_4$. It oxidises ammonia to nitrogen, chromium (III) to chromate, and arsenite to arsenate:

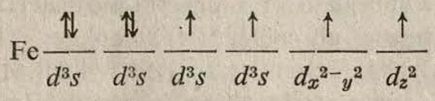
$$2NH_4OH + 2K_2FeO_4 \rightarrow 2Fe(OH)_3 + N_2 + 4KOH$$

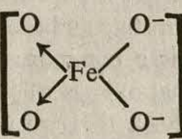
$$Cr(OH)_3 + K_2FeO_4 \rightarrow K_2CrO_4 + Fe(OH)_3$$

It has recently been shown that K_2FeO_4 serves as a selective oxidant for organic compounds. Primary and secondary alcohols are rapidly oxidised to aldehydes and ketones while tertiary alcohols are not affected. A ferrate solution is stable only in the presence of alkali. An acid solution is decomposed:

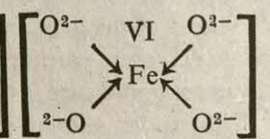
$$4K_2FeO_4 + 20HCl \rightarrow 4FeCl_3 + 3O_2 + 10H_2O + 8KCl$$

The ferrate ion is tetrahedral and is isomorphous with tetrahedral sulphate, selenate and chromate. Thus we have the same bonding pattern as in CrO_4^{2-} (Chapter 26). Iron in tetrahedral geometry may be assumed to have the following electron distribution and structure (28-II*a*) may be written for FeO_4^{2-}.





(28-II*a*)



(28-II*b*)

The lone pairs may be viewed to be donated to two oxygen atoms and the other two d^3s orbitals with one electron each overlap with two O^- ions (two O^- ions getting two electrons from the two M^+ ions of M_2FeO_4). Effectively there remain two unpaired electrons with a moment value of 3.0 B.M. We can also conceive hexavalent iron as a $3d^2$ system and the bonding being effected between an Fe(VI) and four O^{2-} ions (compare CrO_4^{2-}). In this case a filled *p*-orbital of O^{2-} overlaps with an empty d^3s orbital of Fe(VI) (28-II*b*).

28.3.2. Quadrivalent Iron. This oxidation state occurs in o-phenylenebisdimethylarsine (diars) complexes, and in some alkaline earth ferrites. Oxidation of red coloured $[Fe^{III}(diars)_2Cl_2]^+$ compounds by 15*M* HNO_3 gives green to black $[Fe^{IV}(diars)_2Cl_2[^{2+}$. The complex has been isolated as tetrafluoroborate salt. The identity of the compound has been established by bi-univalent electrolytic nature and paramagnetism. Iron (IV) is a $3d^4$ system and a strong d^2sp^3 model will predict two unpaired spins. On the crystal field model a low spin t_{2g}^4 con)figuration will result. Experimental measurement on the compound gives a moment value of 2.87 B.M.

The alkaline earth ferrites $M_2^{II}FeO_4(M^{II} = Sr, Ba)$ or $M^{II}FeO_3$ $(M^{II} = Sr, Ba)$ have been variously called as ferrites, perferrites or ferrates (IV). These are obtained by solid state reaction via heating a mixture of ferric and alkaline earth nitrate in a current of air at ~ 400–600°C or by the oxidation of hexahydroxo ferrates (III) and alkaline earth hydroxide at ~ 800°C in a current of air:

$$M^{II}(NO_3)_2 + Fe(NO_3)_3 \rightarrow M^{II}FeO_3 + 5NO_2 + O_2$$

$$2M_3^{II}[Fe(OH)_6]_2 + 2M^{II}(OH)_2 + O_2 \rightarrow 4M_2^{II}FeO_4 + 14H_2O$$

Although in the above equation FeO_4^{4-} is shown, X-ray crystal structure studies reveal no discrete FeO_4^{4-} ion but only a mixed metal oxide of M^{II} and Fe^{IV}. These compounds are stable in alkaline medium but on acidification evolve oxygen, the iron (IV) being reduced to the ferric state:

$$2M_2^{II}FeO_4 + 14HCl \rightarrow 2FeCl_3 + 4M^{II}Cl_2 + 7H_2O + \tfrac{1}{2}O_2$$

28.3.3. Trivalent Iron. This is the commonest oxidation state of iron and is found in a number of salts and complexes. It is in this oxidation state that the element largely occurs in nature.

An interesting feature of the aqueous chemistry of iron (III) is its ready hydrolysis so that many iron (III) salts in aqueous medium show acid reaction:

$$[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H^+$$

In ~ $1N$ acid solution the ferric salts remain in the hexaaquo form but hydroxo species and other condensed species appear when the pH is raised above 2. On further increasing the pH hydrated ferric oxide is precipitated. The pure hydrated ferric salts, when crystallised from sufficiently acid solutions are, pale violet coloured but when crystallised from a solution of higher pH the compounds are contaminated with a small amount of yellow colloidal ferric hydroxide which suppresses the violet colour.

Ferric Hydroxide: The compound, commonly written as $Fe(OH)_3$, is better represented as $Fe_2O_3.nH_2O$. This is precipitated from a ferric solution on the addition of alkali or ammonia. This is amphoteric although it is weaker as an acid than as a base. Freshly precipitated hydroxide is slightly soluble in hot concentrated alkali, from which solution M^IFeO_2 can be crystallised. These ferrites are green to red in colour. Hexahydroxo iron (III) can be crystallised as the barium or strontium salt by boiling concentrated solutions of strontium or barium hydroxide with ferric perchlorate. $M_3^{II}[Fe(OH)_6]$ $(M^{II} = Sr, Ba)$ are white powders.

Ferric Halides: The fluoride, chloride and the bromide are known. The iodide is not known in a pure state because of the reaction:

$$Fe^{3+} + I^- \rightarrow Fe^{2+} + \tfrac{1}{2}I_2$$

The halides are easily obtained by direct action of the halogens on the metal. Thus $FeCl_2$ is prepared by passing dry chlorine gas through a hot tube containing iron wire. $FeCl_3$ is sublimed at ~300°C and is collected in a bottle attached to the reaction tube. The anhydrous salt is extremely hygroscopic and hence the receiver bottle for $FeCl_3$ during synthesis must be protected with a soda lime guard tube. The compound forms deep red brown plates with a metallic lustre. The bromide is similar. On heating in vacuo ferric halides give ferrous halides. In some organic solvents anhydrous $FeCl_3$ and $FeBr_3$ exist as halo bridged dimers. When crystallised from water the chloride and the bromide give hexahydrates but the fluoride a tetrahydrate. In concentrated HCl solution $FeCl_3$ forms the tetrahedral $[FeCl_4]^-$ but at higher iron (III) concentration and lower H^+ concentration octahedral *trans* diaquo tetrachloro $[FeCl_4(H_2O)_2]^-$ is formed.

Ferric Sulphate: Ferrous sulphate is first obtained by the action of dilute H_2SO_4 on iron scrap:

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$$

This solution is boiled with sufficient nitric acid to oxidise the ferrous iron to the ferric state. The solution is then concentrated and the ferric sulphate crystallised as the heptahydrate:

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

Careful heating of the hydrated salt gives the anhydrous compound. On heating strongly it is decomposed to give ferric oxide and sulphur trioxide.

Ferric Alum: Potassium ferric alum, commonly called *iron alum* is $K_2SO_4.Fe_2(SO_4)_3.24H_2O$ (or $KFe(SO_4)_2.12H_2O$). This is prepared by dissolving equimolar amounts of ferric sulphate and potassium sulphate in minimum amount of hot water and allowing to crystallise. Ammonium ferric alum can similarly be obtained from ammonium sulphate and ferric sulphate.

Potassium Ferricyanide: It is obtained by the oxidation of potassium ferrocyanide by chlorine or by $KMnO_4$ in HCl medium:

$$2K_4[Fe(CN)_6] + Cl_2 \rightarrow 2K_3[Fe(CN)_6] + 2KCl$$

$$5K_4[Fe(CN)_6] + KMnO_4 + 8HCl \rightarrow 5K_3[Fe(CN)_6] + 6KCl + MnCl_2 + 4H_2O$$

Potassium ferricyanide forms dark red crystals which are easily soluble in water. It forms with ferrous salts a deep blue precipitate called *Turnbull's blue*. With ferric salts only a brown colour is obtained. Thus ferricyanide can be used to distinguish a ferrous from a ferric salt. Potassium ferricyanide is isomorphous with $K_3[Mn(CN)_6]$ and $K_3[Cr(CN)_6]$.

Complexes: Dominating geometries are tetrahedral and octahedral. With weak field ligands like Cl^- we have tetrahedral $[FeCl_4]^-$. Most ferric complexes are six-coordinate. Common ferric salts in strongly acid solution occur as $[Fe(H_2O)_6]^{3+}$. With oxalate ion $[Fe(ox)_3]^{3-}$ is formed. Acetylacetone gives red coloured non-electrolytic $[Fe(acac)_3]$. These complexes are all high-spin ($\mu \sim 5.9$ B.M.). Low-spin complexes are formed by very strong-field ligands like dipyridyl, o-phenanthroline, cyanide: $[Fe(depy)_3](ClO_4)_3$, $[Fe(o\text{-}phen)_3](ClO_4)_3$ $K_3[Fe(CN)_6]$ have $\mu \sim 1.7$ B.M. ($t^5_{2g}e_g^0$).

Electronic Spectra: Iron (III) is a $3d^5$ system and hence in the high spin state, like manganese (II), *its transitions are doubly forbidden i.e. both spin forbidden and Laporte forbidden*. Dark colour associated with some complexes (as for example the blood-red thiocyanato complex $[Fe(NCS)_6]^{3-}$ etc.) have ligand—to—metal charge transfer origin.

28.3.4. Bivalent Iron. Since iron is an electropositive element it reacts with non-oxidising acids to liberate H_2 producing ferrous ion in solution.

In aqueous medium the ferrous ion is slowly oxidised by molecular oxygen, as is evident from an appreciation of the following potentials:

$$Fe^{3+} + e \rightleftharpoons Fe^{2+}; \qquad E^\circ = +0.77 \text{ volts}$$

$$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O; \qquad E^\circ = +1.21 \text{ volts}$$

In basic solution the oxidation process is still more enhanced. In the absence of air or oxygen, however, double decomposition or precipitation reactions may be carried out to obtain pure ferrous compounds.

Ferrous Hydroxide: The pure white $Fe(OH)_2$ is precipitated only when scrupulously air-free solutions of ferrous sulphate and sodium hydroxide are mixed. On exposure to air it readily absorbs oxygen and turns dirty green and finally gives hydrated ferric oxide. Ferrous hydroxide is more basic than ferric hydroxide but is still somewhat amphoteric. With acids it gives ferrous salts, and with boiling 50% NaOH (and in the presence of iron powder) it dissolves and gives blue green crystals of $Na_4[Fe(OH)_6]$.

Ferrous Sulphide: This can be obtained by the action of ammoniacal H_2S on a ferrous solution. This is precipitated as a black material. Its solubility product is $\sim 4 \times 10^{-19}$ at 20°C and hence it is not precipitated on the passage of H_2S in acid solution. It is readily oxidised in air when moist. It is a good example of a non-stoichiometric sulphide. The iron-sulphur ratio varies and a ratio of unity is seldom obtained (Fe_6S_7, $Fe_{11}S_{12}$ etc.).

Ferrous Sulphate: This is a vitriol $FeSO_4.7H_2O$. This is easily obtained by the action of H_2SO_4 on metallic iron:

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$$

Laboratory Kipp's apparatus is also a source of ferrous sulphate:

$$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S$$

The Kipp's waste liquid is drawn, heated with little iron filings to neutralise the free acid and to reduce any ferric salt. On cooling light green crystals separate. On a commercial basis iron pyrites is subjected to the action of air and water, when ferrous sulphate and sulphuric acid are produced:

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2FeSO_4 + 2H_2SO_4$$

The solution is treated with iron and then allowed to crystallise. On heating the heptahydrate loses $6H_2O$ to form the monohydrate, which on further heating gives the anhydrous salt. On heating further the salt breaks up to give SO_2, basic ferric sulphate and other products.

Mohr's Salt: This is a schönite type double sulphate, $FeSO_4.(NH_4)_2SO_4, 6H_2O$. This is made by preparing a saturated solution of ammonium sulphate and ferrous sulphate in air-free water containing a few drops of dilute H_2SO_4 at $\sim$ 40°C and allowing to crystallise. Mohr's salt is a pale green compound. It is used in volumetric analysis as a standard ferrous salt and is also employed as a calibrating agent in magnetic susceptibility measurements.

Ferrous Halides: All the four halides are known. The fluoride and the chloride can be obtained by the reduction of ferric fluoride and chloride by hydrogen or by the action of hydrogen fluoride or hydrogen chloride on iron at high temperature. The bromide and the iodide can be synthesised by treating excess iron with bromine or iodine. The hydrated forms ($FeF_2.8H_2O$, colourless; $FeCl_2.6H_2O$, pale green; $FeBr_2.6H_2O$, pale green and $FeI_2.4H_2O$, pale green) can be obtained by dissolving the metal in appropriate aqueous halogen hydracids.

Potassium Ferrocyanide: This is an important hexacyano iron (II) complex. Commercial method of synthesis consists of heating nitrogenous animal refuse such as blood, horn, hoof, leather scrap with iron filings and potassium carbonate and then extracting the product with water. Lemon yellow crystals separate on concentration and cooling. On a laboratory scale the compound can be easily prepared by the action of KCN on a solution of ferrous sulphate. KCN is added till most of the ferrous cyanide, that initially separates, dissolves. The solution is then concentrated and allowed to crystallise:

$$FeSO_4 + 2KCN \rightarrow Fe(CN)_2 + K_2SO_4; \; Fe(CN)_2 + 4KCN \rightarrow K_4[Fe(CN)_6]$$

Ferrocyanic acid $H_4[Fe(CN)_6]$ can be obtained as colourless crystals by treating the lead salt with dilute sulphuric acid. The first two steps of dissociation are those of a strong acid. The ferrocyanide is oxidised by permanganate or chlorine to ferricyanide. Addition of a ferric salt to ferrocyanide produces an intense blue coloured precipitate known as *Prussian blue.*

Sodium Nitroprusside: Nitroprusside ion has the pentacyano nitrosyl ferriate (II) anion. Sodium nitroprusside is prepared by acidifying with HCl a solution containing $Na_4[Fe(CN)_6]$ and $NaNO_2$:

$$Na_4[Fe(CN)_6] + NaNO_2 \rightleftharpoons Na_4[Fe(CN)_5(NO_2)] + NaCN$$

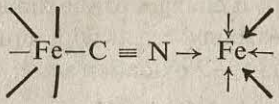
$$Na_4[Fe(CN)_5(NO_2)] + 2HCl \rightleftharpoons Na_2[Fe(CN)_5(NO)] + 2NaCl + H_2O$$

The compound can also be obtained by the action of 1:1 HNO_3 on a concentrated solution of $Na_4[Fe(CN)_6]$. Nitroprusside salts are diamagnetic. In nitrosyl complexes NO functions as a three-electron donor. Its odd electron is first lost to the metal and then NO^+ coordinates as a two-electron donor. Valence of iron in sodium nitroprusside is +2. Alkaline sulphide converts the nitroprusside ion to the purple $[Fe(CN)_5(NOS)]^{4-}$:

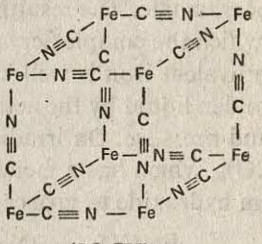
$$Na_2[Fe(CN)_5NO] + Na_2S \rightarrow Na_4[Fe(CN)_5(NOS)]$$

Prussian blue and Turnbull's blue: Treatment of an iron (III) solution with a ferrocyanide gives a blue precipitate known as Prussian blue. A blue precipitate called Turnbull's blue is formed on the addition of a ferricyanide to an iron (II) solution. Although commonly Prussian blue is written as a ferric ferrocyanide, $M^IFe^{III}[Fe^{II}(CN)_6]$, and Turnbull's blue as ferrous ferricyanide, $M^IFe^{II}[Fe^{III}(CN)_6]$, it is most likely that these compounds are the same. The structure consists of a cubic array of iron atoms occupying the corners of a cube and a CN group occupying the middle of each side of the cube. Thus half of the iron atoms face six carbon atoms of CN groups as nearest neighbours and another half of the iron atoms face six nitrogen atoms. The position of the two iron atoms becomes as in

(28-III), and the framework in Prussian blue and related compounds as in (28-IV): Each $[Fe(CN)_6]^{n-}$ anion gets surrounded by six attached cations, and each cation by six $[Fe(CN)_6]^{n-}$ anions. An infinite three dimensional network is thus built up.



(28-III)



(28-IV)

Complexes: The predominant geometry is six-coordinate octahedron. A limited few tetrahedral complexes like $[Fe(Ph_3PO)_2X_2]$, $[Fe(Ph_3PO)_4]^{2+}$ are known. Usual ferrous salts in aqueous acids contain $[Fe(H_2O)_6].^{2+}$. These complexes are all high-spin ($\mu \sim$ 5.0 B.M., $t^4_{2g}\, e_g^2$). Low spin diamagnetic complexes are formed with dipyridyl, cyanide: $[Fe(dipy)_3]X_3$, $K_4[Fe(CN)_6]$ etc.

Electronic Spectra: Iron (II) is a $3d^6$ system. In octahedral geometry the following transitions are possible (Chapter 11; page 276):

high spin : ${}^5T_{2g} \rightarrow {}^5E_g$
low spin : ${}^1A_{1g} \rightarrow {}^1T_{1g}; {}^1A_{1g} \rightarrow {}^1T_{2g}$

Some complexes are given in Table 28.3. The degeneracy of the ${}^5E_g$ state is believed to be lifted by Jahn—Teller effect resulting in split band. Tetrahedral iron (II) has a ${}^5E \rightarrow {}^5T_2$ transition being exemplified by:

$[FeCl_4]^{2-}$, 4.05 kK; $[Fe\,Br_4]^{2-}$, 3.0 kK;
$[Fe(Ph_3AsO)_2Br_2]$, 5.0 kK.

Table 28.3. Electronic Spectra of six coordinate Fe (II) Complexes

Complex (high spin)	${}^5T_{2g} \rightarrow {}^5E_g$ (kK)	Complex (low-spin)	${}^1A_{1g} \rightarrow {}^1T_{1g}$ (kK)	${}^1A_{1g} \rightarrow {}^1T_{2g}$ (kK)
$[Fe(H_2O)_6]^{2+}$	8.3, 10.4	$[Fe(o\text{-}phen)_3]^{2+}$	12.26	—
$[Fe(py)_4Br_2]$	7.75, 10.65	$[Fe(CN)_6]^{4-}$	31.00	37.04

28.3.5. Other Low Oxidation States. Monovalent iron is encountered in the brown ring compound formed in the detection of nitrate radical (via addition of ferrous sulphate solution to a concentrated H_2SO_4 solution of the nitrate). The brown ring compound is usually formulated as $FeSO_4.NO$. In aqueous solution the formula is better expressed as $[Fe(NO)\,(H_2O)_5]\,SO_4$. Solution magnetic measurement gives 3.90 B.M. as the moment value. Remembering that NO is a three electron donor iron should have an oxidation state + 1, that is it should be a $3d^7$ system. The magnetic moment supports this formulation.

Another unipositive iron complex is nitrosyl bis (diethyldithiocarbamato) iron (I), $[Fe\,(NO)\,(S_2CNEt_2)_2]$. This is made by dissolving ferrous sulphate and sodium nitrate in dilute H_2SO_4 and treating the solution with sodium diethyldithiocarbamate. The resulting dark coloured solution is extracted with chloroform from which the complex crystallises on evaporation.

Zerovalent iron is well known in the pentacarbonyl $Fe(CO)_5$. This is obtained as a golden liquid by the action of CO on freshly reduced iron at elevated temperature and pressure. On irradiation with ultraviolet light it changes to the dinuclear $Fe_2(CO)_9$, which has a metal-metal bond. Iron pentacarbonyl reacts with aqueous sodium hydroxide to give carbonylate anion with iron in -2 oxidation state:

$$Fe(CO)_5 + 3NaOH \rightarrow Na[HFe(CO)_4] + Na_2CO_3 + H_2O$$

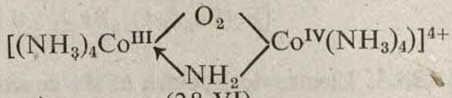
28.4. OXIDATION STATES OF COBALT

28.4.1. Quadrivalent Cobalt. Cobalt (IV) is much too unstable to survive in many compounds. It is a d^5 system and therefore must have either one or five unpaired spins in strong crystal field or weak field respectively. Fluorination of Cs_2CoCl_4 is reported to give Cs_2CoF_6 with a magnetic moment of 2.9 B.M. The moment value does not conform to an easy explanation. Heating a mixture of $Co(OH)_2$ and $Ba(OH)_2$ at ~ 1050°C is said to give Ba_2CoO_4 which has not been sufficiently characterised.

The following polynuclear peroxo bridged cobalt complexes, (28-V) and (28-VI), previously thought to contain both cobalt (III) and cobalt (IV), are now known not to contain any cobalt (IV) but only cobalt (III). It is now believed that the bridging group is not a peroxo group $-O-O-$ but a superoxo group.

$$[(NH_3)_5Co^{III}-O_2-Co^{IV}(NH_3)_5]^{5+}$$

(28-V)



$$[(NH_3)_4Co^{III}\begin{matrix} \diagup O_2 \diagdown \\ \nwarrow NH_2 \diagup \end{matrix}Co^{IV}(NH_3)_4)]^{4+}$$

(28-VI)

28.4.2. Trivalent Cobalt. Due to its high crystal field stabilisation energy cobalt (III) chemistry is dominated by complex formation. It is a $3d^6$ system. In a strong octahedral crystal field it assumes a $t_{2g}{}^6$ low spin (diamagnetic) configuration, which is alternatively expressed as an inner orbital d^2sp^3 complex on valence bond model. In a weak octahedral crystal field four unpaired spins are present. The only high spin complex is the hexafluoro complex $[CoF_6]^{3-}$. An interesting case of a low-spin cobalt (III) complex going over to a high spin form has been reported. The compound $[Co(NH_3)_6]F_3$, which is diamagnetic, changes at 115°C to $[Co(NH_3)_6]$ $[CoF_6]$. This provides a paramagnetic moment (5.2 B.M.). Note that the paramagnetism arises due to the anion only.

$$\underset{\text{diamagnetic}}{2[Co(NH_3)_6]F_3} \xrightarrow{115^\circ C(-6NH_3)} \underset{\text{paramagnetic}}{[Co(NH_3)_6][CoF_6]}$$

Cobaltic Sulphate and Alum: Cobalt (II) sulphate can be oxidised anodically at a platinum electrode in a diaphragmed cell with high current density. The anolyte is $CoSO_4$ in $10N$ H_2SO_4 and is maintained below 10°C. The catholyte is $10N$ H_2 SO_4.

Under these conditions greenish blue crystals of $Co_2(SO_4)_3 \cdot 18H_2O$ appear at the anode. If ammonium sulphate is present alongwith $CoSO_4$ during electrolysis dark blue crystals of cobaltic alum $NH_4Co(SO_4)_2 \cdot 12H_2O$ separate. K, Rb and Cs alums have also been synthesised. The alums are diamagnetic indicating that H_2O molecules are strong enough ligands to force spin pairing in cobalt (III).

Sodium Cobaltinitrite: This is prepared by mixing cold solutions of a cobalt salt and sodium nitrite and acidifying with acetic acid. The solution is then oxidised with a stream of air. The compound crystallises as a yellow material:

$$CoCl_2 + 7NaNO_2 + 2CH_3COOH + \tfrac{1}{2}O_2 \rightarrow Na_3[Co(NO_2)_6] + NO_2 + H_2O + 2NaCl + 2CH_3COONa$$

Sodium cobaltinitrite gives an insoluble precipitate with potassium ion.

Hexamminecobalt(III) Chloride: This is readily made by air-oxidation of an ammoniacal solution of $CoCl_2$ containing NH_4Cl using active charcoal as catalyst:

$$2CoCl_2 + 2NH_4Cl + 10NH_3 + \tfrac{1}{2}O_2 \rightarrow 2[Co(NH_3)_6]Cl_3 + H_2O$$

After the oxidation is over (~2 hrs) the precipitated complex alongwith charcoal is filtered and the complex crystallised from minimum hot water containing little HCl. Active charcoal functions as a catalyst in the shifting of the equilibrium from aquopentamminecobalt(III) to hexammine cobalt (III):

$$[Co(NH_3)_5(H_2O)]^{3+} + NH_3 \xrightarrow{\text{charcoal}} [Co(NH_3)_6]^{3+} + H_2O$$

Instead of air-oxidation, oxidation by H_2O_2 may also be employed.

Roseo Cobaltic Chloride: Air oxidation of $CoCl_2$ in presence of ammonia, NH_4Cl and $(NH_4)_2CO_3$ under appropriate conditions yields crude purple coloured $[Co(NH_3)_5Cl]Cl_2$. This compound is treated with 10% aqueous ammonia to get rose coloured $[Co(NH_3)_5(H_2O)]Cl_3$. Therefore reseo cobaltic chloride should be termed aquopentamminecobalt(III) chloride. This formulatoon is supported by the immediate precipitation of all the chloride by silver nitrate and by the tri-univalent electrolytic nature of the compound.

Purpureo Cobaltic Chloride: The roseo cobalt^{III} chloride $[Co(NH_3)_5(H_2O)]Cl_3$ can be dehydrated at 100°C to produce a purpureo cobaltic chloride. In this compound two chlorine atoms differ from the third. These two chlorine can be precipitated immediately by silver nitrate whereas the third can be precipitated by silver nitrate only on boiling. Hence the compound should be formulated as $[Co(NH_3)_5Cl]Cl_2$.

Cis and trans dichlorotetramminecobalt(III) Chloride:

Cis-isomer: Air oxidation of a mixture of cobalt acetate and sodium nitrite in aqueous ammonia gives a violet solution. The solution is concentrated and treated with ethanol to precipitate *cis*$[Co(NH_3)_4(NO_2)_2]NO_2$. This compound is added in small portions to conc. HCl at −10°C giving a quantitative yield of violet *cis* $[Co(NH_3)_4Cl_2]Cl$.

Trans-isomer: Air oxidation of $CoCl_2$ in presence of NH_4Cl, $(NH_4)_2CO_3$ and ammonia gives purple $[Co(NH_3)_4CO_3]Cl$. This compound is dissolved in water and treated with dilute H_2SO_4 whereby $[Co(NH_3)_4(H_2O)_2]\ (SO_4)_{1.5}$ is formed. The solution is allowed to stand for 24 hours, then chilled in ice and treated with conc. HCl with shaking. Dark green *trans* $[Co(NH_3)_4Cl_2]Cl$ separates after 48 hours.

Tris(biguanide)cobalt(III): Cobalt(II) chloride is added to excess biguanide sulphate and the solution treated with a strong alkali solution. Yellow bis(biguanide)cobalt(II) is precipitated. The mixture is then treated with H_2O_2 and heated on a steam bath. The yellow compound is oxidised to dark red tris(biguanide) cobalt(III) base $[Co(BigH)_3]\ (OH)_3$. The compound can be neutralised with appropriate acids to give red coloured salts $[Co(BigH)_3]X_3$.

Electronic Spectra: Due to a very high *CFSE* in the low-spin state coupled with a comparatively low pairing energy most complexes of cobalt (III) are spin paired. Inspection of Fig 11.11 (Part I; page 276) shows two spin-allowed Laporte-forbidden transitions:

$^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$. In *cis* and *trans* $[CoA_4B_2]^{n+}$ both the excited states are likely to split further. When A and B are widely different in their crystal field strengths, the splitting in the *trans* complex ($^1T_{1g}$ giving $^1A_{2g}$ and ^1E_g) may be sufficient enough to show a total of three bands while the *cis* complex may show only some broadening of the first band. Some spectral data are given in Table 28.4.

Table 28.4. Electronic Spectra of Some Cobalt (III) Complexes :

Complex	$^1A_{1g} \rightarrow {}^1T_{1g}$	$^1A_{1g} \rightarrow {}^1T_{2g}$
$[Co\,(NH_3)_6]^{3+}$	21.2	29.55 kK
$[Co\,(en)_3]^{3+}$	21.3	29.4
$[Co\,(BigH)_3]^{3+}$	21.1	28.4
$[Co\,(dipy)\,(BigH)_2]^{3+}$	21.4	—
$[Co\,(F)\,(H_2O)\,(en)_2]^{2+}$ (*cis*)	20.0	27.8
$[Co(F)\,(H_2O)\,(en)_2]^{2+}$ (*trans*)	17.45, 23.0	28.17

The Tanabe-Sugano diagram shows for the high-spin case only one spin-allowed but Laporte forbidden transition: $^5T_{2g} \rightarrow {}^5E_g$. This transition is Jahn Teller sensitive so that doublet bands (10 and 15 kK) appear for $K_3[CoF_6]$.

28.4.3. Bivalent Cobalt. It is a $3d^7$ system and occurs in octahedral, tetrahedral and square planar stereochemistries. Weak ligands produce tetrahedral geometry. Tetrahedral complexes register a high magnetic moment. Such moments are higher than the spin only moments of three unpaired electrons ($e^4t^3{}_2$ configuration) due to orbital contribution. Octahedral complexes can be high spin (=3 unpaired electrons with orbital contribution) or low spin (= 1 spin). Square planar complexes show one unpaired spin. Examples are: tetrahedral $[CoX_4]^{2-}$ (X = Cl, Br I NCS, etc); octahedral (high spin) $[Co(H_2O)_6]^{2+}$; octahedral (low spin) [Co (diars)$_3$]$^{2+}$; square planar, [Co(DMG)$_2$], [Co(Big)$_2$] etc. Details of their magnetochemistry appear in Chapter 11.

Cobalt Chloride: This may be obtained by dissolving the oxide in hydrochloric acid and crystallising. It forms a pink coloured hexahydrate. The anhydrous salt can be obtained by heating the hexahydrate in a current of dry HCl, by heating the metal in dry chlorine or by dehydrating the hexahydrate with thionyl chloride. The pink colour is due to $[Co(H_2O)_6]^{2+}$, and changes to blue in HCl due to the tetrahedral $[CoCl_4]^{2-}$.

Cobalt Sulphate: It is obtained by dissolving the oxide in sulphuric acid. It is a vitriol $CoSO_4.7H_2O$ and also forms a schönite type double sulphate $(NH_4)_2$–$SO_4.CoSO_4.6H_2O$. The compound is used in cobalt electroplating.

Electronic Spectra: We have noted (Chapter 10; page 240) that in a tetrahedral geometry Laporte forbidden *d–d* transitions are allowed to a greater extent due to *d–p* mixing than is possible in a centro-symmetric octahedral geometry. Hence tetrahedral complexes are more intensely coloured than octahedral complexes: $[Co(H_2O)_6]^{2+}$, pale pink; 550 nm; $\epsilon \simeq 10$; $[CoCl_4]^{2-}$, deep blue; 700 nm; $\epsilon \simeq 600$. The $3d^7$ cobalt (II) in octahedral geometry has the following three spin-allowed but Laporte—forbidden transitions in high spin state (Chapter 11; page 276);

$$^4T_{1g}(F) \rightarrow {}^4T_{2g};\quad {}^4T_{1g}(\mathrm{F}) \rightarrow {}^4A_{2g};.\quad {}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P).$$

In low spin state the ground term is ^2E_g and the following transitions are possible;

$$^2E_g \rightarrow {}^2T_{1g};\quad {}^2E_g \rightarrow {}^2T_{2g}; {}^2E_g \rightarrow {}^2A_{1g};\ {}^2E_g \rightarrow {}^2A_{2g}$$

In a tetrahedral geometry the diagram of the octahedral case is reversed and we get the following transitions:

$$^4A_2 \rightarrow {}^4T_2; {}^4A_2 \rightarrow {}^4T_1(F); {}^4A_2 \rightarrow {}^4T_1(P).$$

$[Co(H_2O)_6]^{2+}$ has bands at 8.1, 16.0 and 19.4 *kK* while blue tetrahedral $[CoCl_4]^{2-}$ shows the second and the third bands at 4.78 and 14.30 kK. The first band is not observed.

28.4.4. Other Low Oxidation States. Cobalt (I) is known in complexes with π-acid ligands. Excess of isocyanide, C = N–R, reacts with cobalt (II) salts in ethanol to form complexes of the type $[Co(CNR)_5]^+$. Bivalent cobalt (II) isocyanide complexes can also be reduced by N_2H_4 or dithionite to give yellow-brown $[Co(CNR)_5]^+$. These complexes are diamagnetic indicating a low spin $3d^8$ system. On valence bond model a trigonal bipyramidal dsp^3 hybridisation is indicated.

Reduction of tris(o-phenanthroline)cobalt(II) perchlorate by borohydride ion in ethanol at $-5°C$ also gives a monovalent cobalt complex $[Co(ophen)_3]ClO_4$.

Zerovalent cobalt is well known in the dimeric carbonyl, $Co_2(CO)_8$, obtained by the action of CO and H_2 on $CoCO_3$ under high pressure and temperature:

$$2CoCO_3 + 2H_2 + 8CO \xrightarrow[120-200°C]{250-300\text{ atm.}} Co_2(CO)_8 + 2CO_2 + 2H_2O$$

This forms orange crystals which melt at 51°C, and can be sublimed in vacuo. There is cobalt-cobalt bond in the compound.

Cobalt carbonyl suffers an interesting disproportionation reaction in presence of isocyanides:

$$Co_2(CO)_8 + 5CNR \rightarrow [Co(CNR)_5]^+[Co(CO)_4]^- + 4CO$$

This reaction indicates that CO is a better low oxidation state stabiliser than CNR. Uninegative cobalt in carbonylate anion can also be synthesised by reduction of $Co_2(CO)_8$ by sodium in tetrahydrofuran:

$$CO_2(CO)_8 + 2Na \xrightarrow{\text{tetrahydrofuran}} 2Na[Co(CO)_4]$$

28.5. OXIDATION STATES OF NICKEL

28.5.1. Quadrivalent Nickel. Dark purple sparingly soluble crystals of Na(K) $NiIO_6.xH_2O$ are formed when nickel (II) sulphate is oxidised by a hot solution of sodium or potassium persulphate in the presence of periodate ion. In the crystal lattice nickel (IV) assumes an octahedral geometry being surrounded by oxygen atoms from neighbouring periodate ions. A polymeric $(NiIO_6)_n$ with stacking of layers will give octahedral $[NiO_6]$ chromophore. A strong field complex for $3d^6$ nickel (IV)($t_{2g}{}^6$; d^2sp^3 hybridisation) would require spin pairing. The small paramagnetism (1.2 B.M.) of the complex is suspected to be due to slight nickel (III) impurities.

A quadrivalent and a trivalent nickel complex of o-phenylenebisdimethylarsine (diars) have been prepared by the following reactions:

$$\begin{tikzcd}
NiCl_2 + 2\ \text{diars} \arrow[r] & [\text{Ni (diars)}_2]Cl_2 \arrow[r, shift left, "Cl_2"] & [\text{Ni(diars)}_2Cl_2]Cl \arrow[l, shift left, "SO_2"] \arrow[d, shift right, "15N HNO_3 + HClO_4"'] \\
 & & [\text{Ni(diars)}_2Cl_2]\,(ClO_4)_2 \arrow[u, shift right, "SO_2"']
\end{tikzcd}$$

$[\text{Ni (diars)}_2]Cl_2$: red, diamagnetic

$[\text{Ni(diars)}_2Cl_2]Cl$: yellow brown, paramagnetic ($\mu = 1.89$ B.M. ($t_{2g}{}^6e_g;d^2sp^3$)

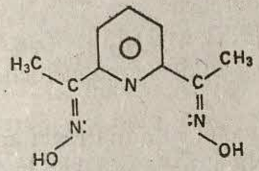
$[\text{Ni(diars)}_2Cl_2]\,(ClO_4)_2$: blue green, diamagnetic ($t_{2g}{}^6$; d^2sp^3).

Chart 28-I. Syntheses of nickel (III) and nickel (IV) o-phenylenebisdimethylarsine complexes.

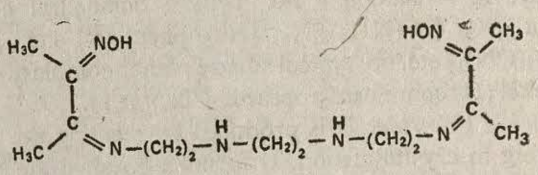
An interesting quadrivalent nickel compound is $K_2[NiF_6]$. This is obtained as red crystals by heating a mixture of $NiCl_2$ (one mole) and dry KCl (2 moles) in a stream of fluorine at 275°C for three hours. The excess fluorine is driven out by flushing with nitrogen. This compound is diamagnetic. On V. B. model it is to be regarded as an inner orbital (d^2sp^3) complex while on crystal field model it is a $t^6{}_{2g}$ spin-paired complex. One might enquire as to how a weak field ligand like F^-

forces spin pairing in $K_2[NiF_6]$ particularly when another $3d^6$ system, namely cobalt (III) gives a paramagnetic ($\mu \sim 5.2$ B.M.) $K_3[CoF_6]$. Although both Ni (IV) and Co (III) in low-spin state have *CFSE* equal to -24 *Dq* in their respective *Dq* units the *Dq* increases sharply with increasing positive charge on the metal ion. The enhanced *Dq* of Ni (IV) helps to overcome the effect of interelectronic repulsion i.e. $10\ Dq > P$. But in $K_3[CoF_6]$ 10 *Dq* is still less than the pairing energy of cobalt (III).

Recently some interesting nickel (IV) complexes with pyridine oximes and oxime schiff bases have been described. Oxidation of aqueous nickel (II) chloride in the presence of 2, 6-diacetylpyridinedioxime ($DAPDH_2$) (28-VII) with $(NH_4)_2S_2O_8$ produces violet needles of [Ni $(DAPD)_2$] with $[Ni^{IV}N_6]$ chromophore. As expected the compound is diamagnetic. Interestingly the Ni-N bonds are shorter by 0.17A than in the corresponding nickel (II) complex $[Ni(DAPDH)_2]$. Similar oxidation of nickel (II) perchlorate in the presence of the schiff base H_2L (28-VIII) gives violet crystals of diamagnetic $[NiL](ClO_4)_2$. The schiff base is obtained by the condensation of biacetylmonoxime with triethylenetetramine. In both the cases nickel (IV) is linked to nitrogen of the oxime group.



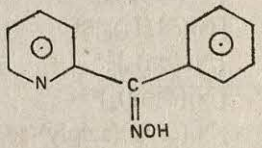
(28-VII)



(28-VIII)

28.5.2. Trivalent Nickel. Certain phosphine complexes $[Ni(R_3P)_2X_2]$ (X = Cl, Br) can be oxidised by ClNO or BrNO to trivalent nickel (III) complexes $[Ni(R_3P)_2X_3]$. These are five-coordinate, non-electrolytes and are monomeric in organic solvents. Their near-zero dipole moment indicates a symmetrical trigonal bipyramidal structure, the three bromine atoms occupying equatorial positions. Their magnetic moments correspond to one unpaired spin.

A yellow brown paramagnetic $[Ni(diars)_2Cl_2]Cl$ is also known (section 28.5.1). Black crystals of $[Ni(BPO)_3]$ are obtained by persulphate oxidation of a mixture of 2-benzoylpyridine oxime (BPOH; 28-IX) and nickel (II) chloride in aqueous medium. The compound has a moment value of 1.75 B. M. with $[NiN_6]$ chromophore. Recently $[Ni(BigH)_2Cl_2]Cl$ and $[Ni(BigH)_2Br_2]Br$ have been obtained as red brown compounds by the oxidation of square planar $[Ni(BigH)_2]Cl_2$ and $[Ni(BigH)_2]Br_2$ with the appropriate halogens in chloroform suspension. Their oxidation potentials are high ($\sim$0.85 volts) and magnetic moments are in the range of low-spin octahedral $3d^7$ nickel (III) (1.72—1.95 B.M).



(28-IX)

28.5.3. Bivalent Nickel. This is a $3d^8$ system. Its chemistry is very rich. Its aqueous solution contains the hexaaquo nickel (II) ion. It forms a vitriol and a schönite type double sulphate. Its rich complex chemistry includes a variety of stereochemistries: tetrahedral, octahedral, square planar, square pyramidal and trigonal bipyramidal. Square planar complexes are diamagnetic (dsp^2 hybridisation or d_{xz}^2, d_{yz}^2, d_z^2, d_{xy}^2) and are yellow to red in colour with [NiN_4] chromophore. Square planar [NiN_2O_2] complexes are mostly green but are yellow to red in some cases. Octahedral and tetrahedral complexes are paramagnetic, the moment values being substantially higher than the spin only moment of two unpaired electrons. The tetrahedral complexes are intense green whereas octahedral complexes are light blue to blue green. Examples of tetrahedral complexes are $[NiX_4]^{2-}$ (X = halogen), [NiL_2X_2] (L = PPh_3 and X = halogen), [NiL_2X_2] (L = $OPPh_3$; X = halogen) etc. Typical octahedral complexes are $[Ni(H_2O)_6]X_2$, $[Ni(en)_3]X_2$, $[Ni(NH_3)_6]X_2$, $[Ni(o\text{-}phen)_3[X_2$ etc. $[Ni(DMG)_2]$, $[Ni(BigH)_2]X_2$, $K_2[Ni(CN)_4]$ etc. are typical square planar complexes. Details of magnetochemistry of nickel (II) complexes appear in Chapter 11.

Nickel Chloride: It is produced by reacting the metal in aqua regia and evaporating to crystallisation. It forms a hexahydrate $NiCl_2.6H_2O$. Alkali hydroxide precipitates apple green $Ni(OH)_2$.

Nickel Sulphate: Nickel hydroxide can be dissolved in dilute H_2SO_4 to a green solution. On crystallisation a vitriol $NiSO_4.7H_2O$ separates,

Electronic spectra: Bivalent nickel is a $3d^8$ system. In octahedral crystal field the ground state is $^3A_{2g}$ and the following spin allowed but Laporte forbidden transitions are possible:

$$^3A_{2g} \rightarrow {}^3T_{2g}(F);\ {}^3A_{2g} \rightarrow {}^3T_{1g}(F);\ {}^3A_{2g} \rightarrow {}^3T_{1g}(\mathrm{P}).$$

Spin forbidden and Laporte forbidden transitions $^3A_{2g} \rightarrow {}^1E_g$ and $^3A_{2g} \rightarrow {}^1T_{1g}$ (F) are very weak indeed. The three spin-allowed transitions for $[Ni(H_2O)_6]^{2+}$ occur at 8.5, 13.8 and 25.3 kK (Table 28.5). It is interesting to note from Fig. 11.11 that in an octahedral field the ^1E_g state never crosses the $^3A_{2g}$ ground state i.e. *it is not possible to have a low-spin nickel (II) complex in a perfectly octahedral geometry.*

Table 28.5. Electronic Spectra of Some Nickel (II) Complexes

Complex	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$;	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$;	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
$[Ni(H_2O)_6]^{2+}$	8.5	13.8	25.3 *kK*
$[Ni(NH_3)_6]^{2+}$	10.75	17.5	28.2
$[Ni(en)_3]^{2+}$	11.2	18.35	29.0
$[Ni(dipy)_3]^{2+}$	12.65	19.2	—
$[Ni(dipy)(salgly)(H_2O)]$	11.10	17.10	
	$^3T_1(F) \rightarrow {}^3A_2$	$^3T_1(F) \rightarrow {}^3T_1(P)$	
$[NiCl_4]^{2-}$	7.55	14.25 *kK*	
$[Ni(Ph_3PO)_2Cl_2]$	7.29	14.29	

Tetrahedral nickel (II) will have the reverse diagram of octahedral nickel (II) so that the following transitions occur:

$$^3T_1(F) \rightarrow {}^3T_2\ ;\ {}^3T_1(F) \rightarrow {}^3A_2\ ;\ {}^3T_1(F) \rightarrow {}^3T_1(P)$$

The first band is at quite low energy but the other two are often detected (Table 28.5).

Note that as demanded by theory tetrahedral complexes have comparatively high absorption ($\epsilon \sim 200$) than octahedral ones ($\epsilon \sim 2$ to 20).

28.5.4. Low Oxidation States. Monovalent nickel complexes are few. Reduction of $K_2[Ni(CN)_4]$ by tin or zinc in alkaline solution or by NH_2OH or $SnCl_2$ in alkaline medium gives a dark red solution in the absence of air. Addition of alcohol precipitates a dark red material of composition $K_2[Ni(CN)_3]$. This red material has also been obtained by the action of sodium or potassium on a solution of $K_2[Ni(CN)_4]$ in liquid ammonia. The compound has strong reducing properties and can liberate hydrogen from water. It rapidly absorbs CO to form pale orange coloured $K_2[Ni(CO)(CN)_3]$. The structure of $K_2[Ni(CN)_3]$ is rather uncertain. Its diamagnetic nature is peculiar for a $3d^9$ system. A dimeric structure with nickel—nickel bond has been proposed to explain the diamagnetism.

Oxidation of tetrakis (triphenyl phosphine) nickel (O), $[Ni(PPh_3)_4]$ by halogens gives monovalent nickel complexes of the type $[Ni(PPh_3)_3X]$ (X = Cl, Br, I). The order of stabilities follows the sequence $Cl < Br < I$. Magnetic moments are in the range 1.9—2.0 B.M. as expected for $3d^9$ systems. Nickel (I) has been stabilised by a few complicated phosphine and arsine donors. Expectedly stabilisation of this oxidation state has been effected mostly through soft donor ligands which can accept back donated electrons from nickel (I) to their vacant antibonding orbitals (cf: Chapter 23).

Zerovalent nickel is very well known in the tetracarbonyl which is obtained by the action of CO on nickel at ordinary temperature and pressure. The reaction is reversible so that at elevated temperature the nickel carbonyl can be decomposed to get pure nickel. It is a colourless liquid (B.P. 43°C).

PCl_3 reacts readily with $Ni(CO)_4$ displacing all the CO groups and thus producing a yellow non-volatile $[Ni(PCl_3)_4]$. Similar reaction between $Ni(CO)_4$ and PF_3 is incomplete but PF_3 reacts readily with finely divided nickel to give $[Ni(PF_3)_4]$. Again under pressure PF_3 can displace all PCl_3 from $[Ni(PCl_3)_4]$ to produce $[Ni(PF_3)_4]$.

Aryl isocyanides (CNR) can also displace all the CO groups from $Ni(CO)_4$ to produce yellow crystalline $Ni(CNR)_4$:

$$Ni(CO)_4 + 4CNR \rightarrow Ni(CNR)_4 + 4CO$$

In absolute ethanol medium o-phenanthroline reacts with $Ni(CO)_4$ to produce ruby red needles of $[Ni(CO)_2(o\text{-phen})]$.

28.6. ISOLATION OF IRON, COBALT AND NICKEL

28.6.1. Iron. Important ores of iron include *haematite* (Fe_2O_3), *magnetite* (Fe_3O_4), *limonite* ($Fe_2O_3.xH_2O$), *siderate* ($FeCO_3$) and *iron pyrites* (FeS_2). A number of steps are involved in the extraction of iron from its ores and its conversion to more useful alloys, namely steels. The following general steps are involved:

1. Reduction of iron oxide ore with CO to *pig iron*.

2. Treatment of the pig iron to remove some undesirable constituents, and addition of some constituents to improve the quality.

3. Tempering or annealing of the product to help develop the required physical properties.

The raw materials used are iron ore (usually haematite), coke, limestone, air and water. The exact method followed in a particular plant is determined by the quality of the raw materials.

The reduction of iron ores to pig iron is carried out in blast furnaces. Blast furnaces are made of steel shell lined with refractory brick. These furnaces generally run to a height of ~ 100 ft. and to a diameter of ~30 ft. Once a blast furnace has been commissioned it is run continuously. Alternate charges of ore, limestone and coke are introduced at the top of the furnace at regular intervals. Near the bottom of the furnace a blast of preheated air is forced into the furnace through water-cooled nozzles called *tuyers*. The coke reacts with the heated air to produce first CO_2 which then reacts at the high temperature to give CO:

$$C + O_2 \rightarrow CO_2 \ ; \ CO_2 + C \rightarrow 2CO$$

As the mixture of limestone, coke and ore descends the furnace the rising CO reduces the iron oxide to the metallic iron. This reduction proceeds in several steps depending on the temperature prevailing at different zones inside the blast furnace. The highest temperature (~1900°C) prevails near the base and the lowest (~200°C) at the top. Following reactions occur as the charge descends:

$$2Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2$$
$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$$
$$FeO + CO \rightarrow Fe + CO_2$$

Alongside the above reactions, limestone and the other impurities in the ore also participate in slag formation. At 480°C limestone breaks down into CaO and CO_2. The CaO now combines with SiO_2 and Al_2O_3 present in the ore to form fusible materials called *slag* which consists of $CaSiO_3$ and $Ca(AlO_2)_2$:

$$CaO + SiO_2 \rightarrow CaSiO_3 \ ; \ CaO + Al_2O_3 \rightarrow Ca(AlO_2)_2$$

The pig iron also reacts to some extent with carbon or with CO to form some iron carbide, called *cementite* (Fe_3C):

$$3Fe + 2CO \rightarrow Fe_3C + CO_2 \ ; \ 3Fe + C \rightarrow Fe_3C$$

The pig iron also carries some phosphorus, silicon and aluminium which are produced by reduction of the impurities.

At the high temperature near the base the pig iron and the slag stay in a fused state forming two layers. The upper layer is the slag and the lower one is pig iron. It is run into sand moulds where it solidifies. Carbon content of pig iron is about 4% in addition to other impurities mentioned above. Due to the impurities the melting point of pig iron is ~1200°C, much lower than that of pure iron (1535°C). Pig iron is hard, brittle, and hence is unsuitable for structural purposes. This has therefore to be treated further to produce steel and other alloy steels with desired properties. However the comparatively low melting point and its satisfactory fluidity makes pig iron suitable for manufacture of castings which are not subjected to sudden shocks or strains.

Iron-Carbon Alloys: Pig iron may be processed further to give products of three major types: *cast iron, wrought iron and steel.* All the forms are alloys of carbon and iron alongwith other minor constituents. They differ in their carbon contents. Iron-carbon alloys containing $> 1.7\%$ carbon by weight are known as *cast iron.* Commercial varieties of cast iron have carbon content ranging from 2 to $\sim 4\%$. *Wrought iron* contains 0.02—0.04% carbon but 1—2% ferrous silicate slag. An iron-carbon alloy with $< 1.7\%$ carbon, and which can be hardened by quenching is generally called *steel.* Because of their low carbon content wrought iron cannot be hardened by quenching.

Iron can assume two crystalline forms: at temperatures upto ~910°C the metal assumes an α-form which has a body centred cubic lattice. From 910°C to 1400°C it assumes a γ-form which has a cubic close packed structure. Beyond 1400°C the γ-form again changes to the α-form. Above 900°C all carbon-iron alloys form an interstitial solid solution of carbon in γ-iron, this solid solution being called *austentite.* The maximum solubility limit of carbon in γ-iron is 1.7% by weight. The presence of carbon in solid solution stabilises the γ-iron structure and retards the transition to the γ-form. On slow cooling of the solid alloy the γ-iron changes at ~700°C to the α-form The solubility of carbon in the α-form is very low and hence excess carbon separates out of the solid solution as cementite (Fe_3C). Thus an alloy composed of α-iron plus little carbon (ferrite), and cementite results. But the transformation of the austentite to the α-iron and cementite in the solid state can occur only at a relatively high temperature (900—1400°C). Therefore, if an iron-carbon alloy is rapidly cooled the transition from austentite to a mixture of α-iron and cementite cannot occur, although most of the γ-iron change to the α-form. Some austentite is still retained. The product therefore is a solid solution of cementite in α-iron. Since the solubility of cementite in α-iron is very low the resulting solid solution is supersaturated. Crystals of this supersaturated alloy are extremely hard. Hence rapid cooling of pig iron yields a very hard alloy. Softer alloy may be obtained by slower cooling, allowing a larger amount of cementite to crystallise from the solid solution. The phase relationships in the iron—carbon system are given in Chart 28-II.

Austentite (solid solution of carbon in γ-Fe)
↓ slow cooling to 700°C
Mixture of ferrite (solid solution of carbon in α-Fe) and cementite (Fe_3C)
↓ reheat
Austentite + graphite

Austentite
↓ rapid cooling to 150°C
supersaturated solid solution of carbon in α-Fe + some retained austentite
↓ tempering at ~ 250°C
Mixture of ferrite and cementite

Chart 28-II. Changes in the iron-carbon system with variation in temperature.

Steel: Steels have lower percentages of carbon and other impurities than do the pig iron. Hence manufacture of steel from pig iron is essentially a purification step. Purification involves oxidation of the impurities by atmospheric air, and fortunately most of the impurities can be oxidised before much oxidation of iron can occur. The purification is carried out by two techniques: Bessemer process and the Open-hearth process.

The Bessemer Process: The process was introduced by Henry Bessemer in 1856. The impurities in pig iron are oxidised rapidly by injecting a stream of air or air plus oxygen under pressure whereby Si, Mn, C, etc. are oxidised. The Bessemer converter is essentially an egg-shaped steel vessel lined on the inside with refractory brick. To aid the loading of pig iron and the unloading of steel the converter is set on *trunions* so that it can be moved, as desired, from a standing vertical position to a horizontal position. Air is forced through small inlets at the bottom. It generally handles about 30 tons of pig iron.

The converter is set to a horizontal position while receiving the molten pig iron from blast furnace. It is then changed to the vertical position, and air and oxygen under pressure of ~10—25 lbs is blown through. Silicon, manganese and little of the iron are rapidly oxidised, which is exhibited by sparks and brown fumes.

$$\mathrm{Si + O_2 \rightarrow SiO_2;\ 2Mn + O_2 \rightarrow 2MnO;\ 2Fe + O_2 \rightarrow 2FeO}$$

The silica reacts with MnO and FeO to form slag:

$$\mathrm{MnO + SiO_2 \rightarrow MnSiO_3;\ FeO + SiO_2 \rightarrow FeSiO_3}$$

The carbon present in pig iron as Fe_3C is also oxidised;

$$\mathrm{2Fe_3C + O_2 \rightarrow 6Fe + 2CO}$$

The CO is oxidised to CO_2, which is observed in a majestic column of blue flame about 20—30 ft. high from the mouth of the converter. The purification is generally over within twenty minutes. As soon as the CO flame dies down air injection is stopped to prevent any further oxidation of iron. The converter is tilted to take some calculated amount of carbon (as charcoal) and manganese (added as *spiegeleisen*; 15—20% Mn, the rest being iron). The latter serves to reduce the iron that had been oxidised, the MnO forming slag with SiO_2. The molten Bessemer steel is then poured into moulds from which high quality pipes, etc can be made.

The Open Hearth Process: This is the currently used technique of producing high quality steels from pig iron. The open hearth is a shallow saucer-like hearth that contains the pig iron. A temperature ~ 1600°C is maintained in the hearth by making a suitable mixture of air and a gas (producer gas, coal gas etc) burn over the surface of the molten pig iron. To economise on the fuel the mixture of air and the gas is used in a regenerative system of firing. The open hearth furnace contains two sets of brick *checkers* on each side. The fuel gas and air are led into the furnace through one set of checkers and the exhaust gases pass out through the other set. The flow of the fresh gas and air is next reversed so that the incoming mixture is preheated by the already hot checkers. The open hearth is made of cast iron being lined on the inside by dead-burnt magnesium oxide brick (*basic open hearth*) or by silica (*acidic open hearth*).

For pig iron with high phosphorus and sulphur content a basic open hearth is used. Silicon, phosphorus and sulphur of the pig iron react with the basic lining of the hearth to form a slag. Sometimes limestone is added to help in the slag formation. In practice the charge of an open hearth contains in addition to pig iron some iron ore (Fe_2O_3), scrap iron, scrap steel and limestone. The iron ore, scrap iron/steel and limestone are first heated for about two hours. Molten pig iron is next added. The silicon, manganese and phosphorus are readily oxidised and form a slag ($CaSiO_3$, $MnSiO_3$, $FeSiO_3$, etc). Carbon is then slowly oxidised and the evolution of CO keeps the charge in a well stirred condition:

$$2C + O_2 \rightarrow 2CO; 3Fe_3C + Fe_2O_3 \rightarrow 11Fe + 3CO$$

The open hearth purification proceeds slowly (~8—10 hours) so that the progress can be followed by actual analysis of the steel. More iron ore is added till the carbon content is brought down to the desired level. Requisite quantity of ferromanganese and other alloys are then added to have the desired product. The slag being lighter than the steel forms the upper layer. The molten steel and the slag are removed from the bottom through tap holes.

Acidic open hearth is seldom used in steel making. It is preferred for the manufacture of certain special types of steel from steel scrap.

The Bessemer process is very rapid although it results in a steel of lower quality. The open hearth process, on the other hand, is slow but can handle larger quantity of charge. The open hearth process also produces better quality steel, and it is also costlier because of large fuel consumption. This process also allows a wider selection of crude charge: pig iron, scrap steel/iron etc.

28.6.2. Cobalt. The element almost always occurs in nature in combination with arsenic and sulphur. Nickel, copper, silver and iron also accompany cobalt in the ores. The important sources are: *smaltite* ($CoAs_2$); *cobaltite* ($CoAsS$); *linnaeite* (Co_3S_4) and *erythrite* ($3CoO.As_2O_5.8H_2O$). Many cobalt ores carry worthwhile amounts of silver.

There are many variations in the extraction procedures depending on the quality of the ore. Arsenical ores are heated alongwith coke and limestone in small blast furnace whereby three layers of fused mass are formed. The top layer consists of earthy materials of the ore, and is rejected. The middle layer is fused arsenides of cobalt, nickel, iron and copper. The bottom layer consists of easily reducible metals like silver and copper. The middle layer is then roasted to eliminate arsenic (and some sulphur) and oxidise the iron. The roasted material is treated with dilute H_2SO_4 to dissolve cobalt, nickel, copper and iron as sulphate. The iron is further oxidised to the ferric state by sodium chlorate. The solution is next treated with scrap iron to precipitate copper. Ferric hydroxide is precipitated by lime and then $Co(OH)_3$ by the addition of sodium hypochlorite. $Co(OH)_3$ is heated to the oxide Co_3O_4 which is finally reduced with charcoal at 1000°C to the metal.

$$CoSO_4 + 2NaOH \rightarrow Co(OH)_2 + Na_2SO_4$$

$$2Co(OH)_2 + NaOCl + H_2O \rightarrow 2Co(OH)_3 + NaCl$$

$$Co(OH)_3 \xrightarrow{\text{heat}} Co_3O_4;\ Co_3O_4 \xrightarrow[\text{heat}]{C} Co$$

Traces of nickel in cobalt can be removed as volatile $Ni(CO)_4$ by the action of CO on the metal at ~50°C. At this temperature and at ordinary pressure no cobalt carbonyl is formed. Electrolysis of cobalt formate in formic acid solution produces 99.9% pure cobalt.

28.6.3. Nickel. Like cobalt, nickel also occurs as sulphide and arsenide. The principal ores are *nickelite* (Ni As), *garnierite* (Ni, Mg) $SiO_3.xH_2O$ and *pentlandite* (Ni, Cu, Fe)S. The metallurgy differs considerably with the composition of the ore. The Sudbury ores (of Ontario, Canada) which contain iron and copper sulphides in addition to nickel sulphides are smelted in a blast furnace with coke and fluxing material (limestone and silica). The iron mostly passes into a fusible slag $FeSiO_3$. Nickel and copper are still in the form of sulphide, and some FeS still persists. The product (called *matte*) is then taken to a Bessemer converter, mixed with SiO_2 and a blast of air is turned on. The sulphur goes to SO_2 and FeS to FeO which then forms the slag. The matte now contains the sulphides of nickel and copper.

The nickel-copper sulphide matte is now roasted to get NiO and CuO. On treatment with dilute hot H_2SO_4 only copper oxide dissolves and by concentration copper sulphate is recovered. The almost insoluble NiO is then treated with water gas ($CO + H_2$) at 300°C to reduce NiO to metallic nickel. The resulting mass is then reacted with CO at ~50°C converting nickel metal to volatile Ni (B.P. 43°C). The nickel tetracarbonyl is then led through tubes maintained at ~200°C, when pure nickel is deposited;

$$Ni + 4CO \underset{200^\circ C}{\overset{\sim 50^\circ C}{\rightleftharpoons}} Ni(CO)_4$$

Pure nickel is also obtained by an electrolytic puocedure. Impure NiO is cast into plates to serve as anodes. The cathodes are essentially of pure metal. Copper or iron plates covered with graphite coating have also been used as cathodes. Electrolysis is carried out in lead-lined tanks containing nickel sulphate and boric acid solution (as buffer) at pH ~ 5—6. If the solution is sufficiently acid hydrogen is liberated at the cathode in preference to discharge of nickel.

28.7. USES OF IRON, COBALT AND NICKEL

Iron: Iron and steel are the very basis of modern civilisation. Pure iron is acted upon by atmospheric air and CO_2 and moisture to form hydrated ferric oxide, commonly known as rust. The hydrated oxide is porous and hence the entire metal is slowly destroyed. When some other element in addition to carbon is present in steel in quantity so as to modify the properties, the product is called *alloy steel*. Many hundred varieties of alloy steels are known, and are used for a variety of purposes. Some important alloy steels are noted in Table 28.3.

Cobalt: It is mainly used in very hard corrosion resistant alloy steels known as *stellites*. These are composed of cobalt, iron and one or more of the metals W, Ni, Cr and Mo. These make good surgical instruments and high-speed cutting tools. Cobalt-containing steels and other cobalt alloys (Al, Ni and Co) are used in making permanent magnets.

Cobalt-60 isotope is used as a radiotherapeutic agent. This isotope emits two gamma rays accompanied by beta radiation. The beta radiation can be cut off by 0.3 mm steel without reducing the gamma intensity. For use in therapy special devices for holding the cobalt-60 source with radiation protection provisions and suitable focussing are available. Cobalt-60 is also finding use in food preservation.

Table 28.3. Alloy Steels

Alloying Element	Approximate Composition	Properties and Uses
Manganese	>10% Mn; 1.0–1.4%C	Very hard; used in rails, conveyer chains, rock crushers.
Nickel	3% Ni; 0.3% C	Increased ductility and strength; used in propeller shafts, gear steel, steel castings.
Chromium	4–10% Cr; <0.2% C	Increased resistance to corrosion; increased hardness; used for making high temperature and high pressure equipments.
Chromium-Nickel	17–19% Cr; 7–9% Ni; ~0.2% C.	Stainless steel; high resistance to corrosion and increased strength.
Chromium-Vanadium	~1% Cr; ~0.15%V; 0.1–1.0%C.	Used for balls, ball bearings and tools.
Tungsten-Chromium	18% W; 4% Cr; 1% C.	High speed tool.

Nickel: Principal uses are in the manufacture of special alloys: *stainless steels* (17–19% Cr; 7–9% Ni; 0.2% C; rest iron); *german silver* (5–45% Zn; 5–30% Ni; rest copper); *monel metal* (~67% Ni; ~30% Cu and small amount of Fe). Heat resistant alloys include *nichrome* and *chromel* which contain nickel, chromium and sometimes iron.

28.8. ANALYTICAL REACTIONS OF IRON, COBALT AND NICKEL

Iron: Iron precipitates as hydrated ferric oxide alongwith $Cr(OH)_3$ and $Al(OH)_3$. The latter two are easily brought to solution by Na_2O_2 in NaOH solution as chromate and aluminate. Ferric iron is then detected by the red colour with thiocyanate solution or by the Prussian blue precipitate with ferrocyanide.

Iron (III) is usually determined volumetrically by reduction to the ferrous state by excess stannous chloride (the excess being removed by $HgCl_2$) and titrating the ferrous iron by $KMnO_4$ or by $K_2Cr_2O_7$. In the latter case diphenylamine is used as an indicator. Gravimetrically it is precipitated as hydrated ferric oxide and ignited to Fe_2O_3 and weighed.

Cobalt: This appears in group IIIB of the qualitative scheme of analysis. The sulphides of Mn, Zn, Co and Ni are precipitated in ammoniacal medium. Cobalt is finally detected by its blue colour with thiocyanate ($[Co(NCS)_4]^{2-}$). The colour may be extracted into amyl alcohol. The element can also be detected in the presence of sodium nitrite, acetic acid and potassium ion as the yellow sparingly soluble $K_3[Co(NO_2)_6]$.

For gravimetric estimation cobalt compounds may be decomposed to oxide, the oxide dissolved in HCl, then converted to sulphate with a few drops of H_2SO_4 and finally anhydrous $CoSO_4$ obtained at 550°C and weighed. Alternatively cobalt (II) may be precipitated in presence of thiocyanate and mercury (II) as $Hg[Co(NCS)_4]$ and weighed.

Nickel: This is detected and also quantitatively estimated as red coloured bis(dimethylglyoximato)nickel (II) in slightly ammoniacal medium. Small amounts of cobalt are retained in solution under the same condition.

In presence of cyanide $K_2[Ni(CN)_4]$ and $K_4[Co(CN)_6]$ are formed. On boiling cobaltocyanide is oxidised to cobalticyanide but the nickel complex remains unchanged:

$$4K_4[Co(CN)_6] + 2H_2O + O_2 \rightarrow 4K_3[Co(CN)_6] + 4KOH$$

Sodium hydroxide and bromine are then added when the nickel complex decomposes and black higher oxides of nickel are formed. The yellow cobalticyanide remains unaffected.

28.9. GENERAL CONSIDERATIONS OF THE PLATINUM METALS

The members of the second and the third triads of group VIII namely ruthenium, rhodium, palladium, and osmium, iridium, platinum are together known as the platinum metals. These are all rare elements, their sum-total abundance in the earth's crust is $\sim 2 \times 10^{-5}\%$. The platinum metals occur together with other noble metals such as copper, silver and gold.

We have earlier noted that although we find the members of group VIII as three triads, in fact a vertical relation is more realistic. Again these vertical relations are stronger between corresponding members of the second and the third triad than it is between the members of the first triad and the second triad. Thus the pairs Ru and Os, Rh and Ir, and Pd and Pt are quite close in their chemistries.

The probable electronic configurations of the elements alongwith atomic radii, ionisation potentials, etc. appear in Table 28.4. Note that all the six elements have almost the same atomic size. This is one reason for the platinum metals showing comparable chemical behaviour. General similarities are observed in their having high ionisation potentials and high positive standard electrode potentials for the M^{2+}/M couples. All these elements have a large number of binary compounds namely oxides, sulphides and halides. Their small atomic size and particularly the very small ionic size lead expectedly to a dominant complex chemistry. Besides forming the usual sigma-bonded complexes with common ligands like H_2O, halides, nitrogen and sulphur donor ligands they are also quite capable of forming an extensive series of π-complexes. With the exception of Pd and Pt they all form binary carbonyls. All the platinum metals, however, form carbonyl halides, and other π-bonded complexes with isocyanides, mixed complexes with π-bonding ligands, etc. Ruthenium forms a number of nitrosyl complexes. A molecular nitrogen complex of ruthenium ($[Ru(NH_3)_5\ (:N \equiv N:)]^{2+}$) is known. Complexes with R_2S, R_3P and R_3As ligands are also known. Finally platinum forms interesting complexes with acetylene, ethylene and also forms a Pt-C bonded acetylacetonate complex.

Table 28.4. Electronic Configurations and Some Properites of the Platinum Metals

Element	Atomic Number	Electronic Configuration	First I.P. (*ev*)	$E°$, (volts) $M^{2+} + 2e \rightleftharpoons M$
Ruthenium	44	$[Kr]4d^7 5s^1$	7.36	+0.45
Osmium	76	$[Xe]4f^{14}5d^6 6s^2$	8.70	+0.85
Rhodium	45	$[Kr]4d^8 5s^1$	7.46	+0.60
Iridium	77	$[Xe]4f^{14}5d^7 6s^2$	9.00	+1.1
Palladium	46	$[Kr]4d^{10}$	8.33	+0.987
Platinum	78	$[Xe]4f^{14}5d^9 6s^1$	9.00	+1.20

Table 28.5. Some More Properties of the Platinum Metals

Element	Atomic Radius (A)	Ionic (M^{2+}) Radius (A)	M.P. (°C)	B.P. (°C)	Density (gm/ml)
Ruthenium	1.34	. . .	2250	4900	12.2
Osmium	1.35	. . .	3000	5500	22.5
Rhodium	1.34	. . .	1970	4500	12.4
Iridium	1.36	. . .	2410	5300	22.4
Palladium	1.37	0.80	1560	3980	11.9
Platinum	1.38	0.82	1770	4530	21.4

There are however wide variations in their chemistries. The variations arise due to varying stabilities of the different oxidation states and stereochemistries. One particular feature of the elements of the second and the third triads compared to those of the first triad is to be noted: the compounds of the later triads are more easily spin paired than those of the first triad (Chapter 22).

Very many oxidation states are known with the platinum metals. These are given below, the states in bold numbers being the most stable and best known. The italicised states are the next best known.

Ruthenium	+ 8	+ 7	+ 6	+ 5	+ 4	+ 3	*+ 2*		0
Osmium	+ 8	+ 7	+ 6	+ 5	**+ 4**	*+ 3*	+ 2		0
Rhodium			+ 6		+ 4	**+ 3**		+ 1	0
Iridium			+ 6		**+ 4**	**+ 3**		+ 1	0
Palladium					+ 4		**+ 2**		0
Platinum					**+ 4**		**+ 2**		0

28.10. COMPARISON OF NICKEL, PALLADIUM, PLATINUM AND OXIDATION STATES OF PALLADIUM AND PLATINUM

Nickel, palladium and platinum form a vertical group. Palladium and platinum have many similarities. With these two elements + 2 and + 4 states are well known, particularly with platinum. Compared to nickel some interesting differences exist:

1. In nickel the + 2 state is the stablest but + 3 and + 4 states are also known. With palladium + 2 state is also the commonest. With platinum + 2 and + 4 states are equally common.

2. Complexes of + 2 palladium and + 2 platinum are square planar. Depending on the nature of the ligands square planar, tetrahedral, square pyramidal, trigonal bipyramidal or octahedral stereochemistries are possible with + 2 nickel.

3. All + 2 palladium and platinum complexes are low-spin square planar whereas + 2 nickel complexes are low-spin diamagnetic only in combination with strong coordinating ligands. In tetrahedral and octahedral geometries + 2 nickel complexes are always paramagnetic (two unpaired spins).

Addition of suitable coordinating ligands perpendicular to the square plane of certain diamagnetic square planar nickel (II) complexes may give rise to tetragonal distortion. Depending on the extent of destabilisation of the d_{z^2} orbital such tetragonal distortion may lead to *spin state equilibrium*. $3d^8$ nickel (II) may have all the eight electrons paired in the four lower energy orbitals $d^2{}_{xz}$, $d^2{}_{yz}$, $d^2{}_{xy}$ and $d^2{}_{z^2}$ giving a low-spin state, else there may be two unpaired spins: $d^2{}_{xz}$, $d^2{}_{yz}$, $d^2{}_{xy}$, $d^1{}_{z^2}$, $d^1{}_{x^2-y^2}$ giving a high-spin state. Such equilibria has been found to be dependent on the donor strength of the additional ligand and temperature. It is remarkable that spin state of square planar Pd(II) and Pt (II) remain unperturbed by additional ligands.

4. Nickel (II) complexes undergo fast substitution reactions whereas the reactions of palladium (II) and particularly of platinum (II) are slow.

5. Evidences of coordination numbers 5 and 6 for + 2 palladium are meagre. These coordination numbers are also rare for + 2 platinum. Platinum (IV), however, assumes six coordination.

6. No palladium/platinum analogues of nickel tetracarbonyl are known. However, other zerovalent complexes $[Pd(PF_3)_4]$, $[Pt(PF_3)_4]$ corresponding to $[Ni(PF_3)_4]$ are known.

7. For nickel (II) the stability order of the halo complexes is $F^- > Cl^- > Br^- > I^-$ while that of the Pd (II) and Pt (II) complexes is $I^- > Br^- > Cl^- > F^-$. This order follows from our discussion on hard and soft acids and bases (Part I), Nickel (II) is a borderline acid while palladium (II) and platinum (II) are distinctly soft.

8. Square planar platinum (II) complexes are famous for *trans effect*. Trans effect is the ability of a coordinated group to labilise a group *trans* to itself for substitution reactions. Such *trans* effect is weak in square planar palladium (II) and practically unknown in nickel (II) complexes. The high lability of nickel (II) complexes probably explains the absence of *trans effect*.

Tables 28.6 gives examples of representative compounds in different oxidation states. Table 28.7 records the halides.

Table 28.6. Representative Compounds of Palladium and Platinum in different Oxidation States

Element	Oxidation State				
	+6	+5	+4	+2	0
Palladium	...	...	$M_2[PdF_6]$	$(PdCl_2)n$, $[Pd(NH_3)_4]^{2+}$	$[Pd(PF_3)_4]$
Platinum	PtF_6	$(PtF_5)_4$	$H_2[PtCl_6]$	$[Pt(NH_3)_4]^{2+}$, $[PtCl_4]^{2-}$	$[Pt(PF_3)_4]$

Table 27.7. Halides of Palladium and Platinum

Element	Oxidation State			
	+6	+5	+4	+2
Palladium	...	...	PdF_4 (brick red)	PdF_2 (violet) $PdCl_2$ (red) $PdBr_2$ (red) PdI_2 (black)
Platinum	PtF_6 (dark red)	$(PtF_5)_4$ (deep red)	PtF_4 (yellow brown) $PtCl_4$ (red brown) $PtBr_4$ (brown black) PtI_4 (brown black)	$PtCl_2$ (black) $PtBr_2$ (brown) PtI_2 (black)

28.10.1. Hexavalent Platinum. The only representative is PtF_6. Platinum wire on being ignited in fluorine gives red vapours of PtF_6(M.P. 61°C; B.P. 69°C). PtF_6 is very unstable and is a virulent oxidant. It is noteworthy that with PtF_6 Bartlett succeeded in extracting electrons from O_2 molecule and xenon atom to produce crystalline derivatives, $O_2^+[PtF_6]^-$ and $Xe[PtF_6]$. (page 201).

28.10.2. Pentavalent Platinum. The only representative is the tetrameric $(PtF_5)_4$. The compound is obtained as deep red product (M.P. 80°C) by fluorination of $PtCl_2$ at 350°C.

28.10.3. Quadrivalent Palladium and Platinum. Platinum (IV) is far more common than palladium (IV). Palladium (IV) is known in PdF_4 (no other tetrahalides exist), in hexahalo palladium (IV) complexes $[PdX_6]^{2-}$ and in some tetrahalodipyridines. PdF_4 has been obtained in two steps: (*a*) $PdBr_2$ is reacted with liquid BrF_3 to give $Pd[PdF_6]$ and then (*b*) $Pd[PdF_6]$ is further fluorinated by fluorine under pressure at ~ 150°C to get brickred PdF_6. This is readily hydrolysed by water to give expected products such as HF, O_2, O_3 and PdF_2. The hexahalo complexes $[PdX_6]^{2-}$ (X = F, Cl, Br, I) are obtained by the oxidation of $[PdX_4]^{2-}$ solution by the halogens. The colour varies from yellow-orange to red black on changing from fluorine to bromine. On heating they lose halogen and revert to $[PdX_4]^{2-}$. Tetrachlorodipyridinepalladium(IV) $[Pdpy_2Cl_4]$ is obtained as deep yellow powder when a chloroform suspension of $[Pdpy_2Cl_2]$ is treated with chlorine. The compound is unstable and loses chlorine on storing.

Platinum (IV) has an extensive chemistry. All four PtX_4 tetrahalides are known as also a large number of complexes. The tetrafluoride can be obtained by fluorination of $PtBr_4$. The tetrachloride, tetrabromide and the tetraiodide are obtained by the direct interaction of the halogens with platinum at elevated temperatures: ~250°C for $PtCl_4$ and ~150°C for Pt Br_4 sand PtI_4. Structures of these compounds are little known.

Chloroplatinic acid $H_2[PtCl_6]$: It is obtained by dissolving the metal in aqua regia and evoporating with HCl to remove the nitric acid:

$$2HNO_3 + 8HCl + Pt \rightarrow H_2[PtCl_6] + 2ClNO + 4H_2O$$

It is a strong acid and forms alkali and ammonium salts. Heating of H_2PtCl_6 in a current of chlorine gives $PtCl_4$, which provides $PtCl_2$ on heating at ~300°C:

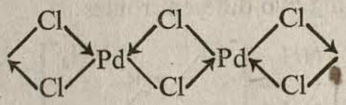
$$H_2[PtCl_6] \rightarrow PtCl_4 + 2HCl \ ; \ PtCl_4 \rightarrow PtCl_2 + Cl_2$$

$M_2[PtF_6]$ compounds are obtained by the action of fluorine on $M_2[PtCl_6]$. An extensive series of ammine complexes are known with platinum (VI): $[PtL_6]X_4$, $[PtL_4X_2]X_2$ (L = monodentate ammine), etc are known. In all complexes Pt (IV) assumes a coordination number six.

28.10.4. Bivalent Palladium and Platinum. This oxidation state is known in all the four dihalides and in an impressive list of complexes. The difluoride is obtained by the following reduction reaction;

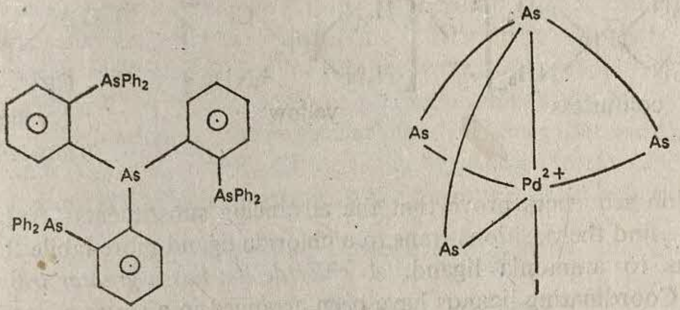
$$PdBr_2 \xrightarrow{BrF_3} Pd[PdF_6] \xrightarrow[\text{reflux}]{SeF_4} PdF_2 + SeF_6$$

The chloride is made by the action of chlorine on the metal at red heat. The anhydrous compound has an infinite chloro bridged chain (28-X):



(28-X)

The anhydrous compound is insoluble in water but dissolves readily in presence of alkali halide (say LiCl) or HCl due to the formation of $[PdCl_4]^{2-}$. The tetrachloropalladate (II) is the starting material for all its complexes. Its complexes are all square planar and diamagnetic (dsp^2 hybridisation). Host of complexes $[Pd(DMG)_2]$, $[Pd(NH_3)_4]X_2$, $[Pd(en)_2]X_2$, $[Pd(BigH)_2X_2$ etc. are known. Recently several claims have been made for five coordinate palladium (II). For example the tetradentate arsine ligand tris (o-diphenylarsinophenyl) arsine (QAS) gives [Pd(QAS)X]X, (28-XI) which behaves as 1:1 electrolyte in nitrobenzene.



(28-XI)

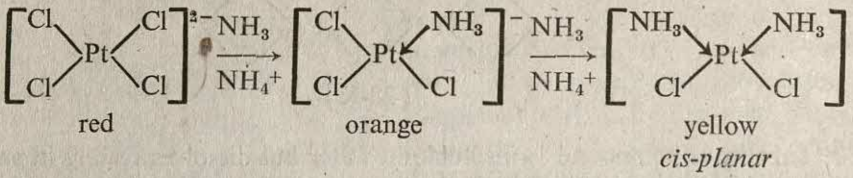
Platinum (II) chloride is obtained by thermal decomposition of $PtCl_4$. The compound has a structure different from that of $PdCl_2$.$PtCl_2$ forms a metal cluster compound Pt_6Cl_{12} where the six platinum atoms occupy the six points of an octahedron and the twelve edges of the octahedron are occupied by the twelve bridging chlorine atoms. Like $PdCl_2$ this too is insoluble in water but dissolves readily in HCl due to the formation of $[PtCl_4]^{2-}$. One of the best known examples of this anion is the *Magnus' green salt* $[Pt(NH_3)_4]$ $[PtCl_4]$. A whole series of complexes, from bipositive cationic ones to binegative anionic ones, are known: $[PtL_4]^{2+}$, $[PtL_3X]^+$, *cis/trans* $[PtL_2X_2]$, $[PtLX_3]^-$ and $[PtX_4]^{2-}$ (L = neutral monodentate and X = uninegative monodentate). Besides neutral inner complexes are also known: $[Pt(acac)_2]$, $[Pt(DMG)_2]$ etc.

Although platinum (II) has square planar geometry in most complexes, a few claims have been made for coordination numbers 5 and 6. One such complex is [Pt(QAS)X]X (cf. 28-XI).

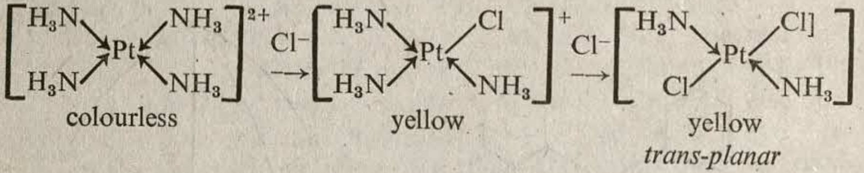
The Trans Effect: An account of platinum (II) chemistry is incomplete without a brief reference to *trans effect*. Synthetic and structural studies on substitution reactions in square planar platinum (II) have revealed that certain coordinated ligands induce substituent groups to occupy positions *trans* to themselves

i. e. certain ligands have a trans-labilising influence. Dichlorodiammineplatinum (II) can exist as two geometrical isomers: *cis planar* and *trans planar* forms. These are obtained by following two different routes:

(*a*)



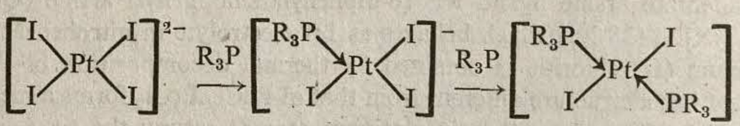
(*b*)



The reaction sequences prove that the advancing substituents—NH_3 in (*a*) and Cl^- in (*b*)—find the positions trans to a chloride ligand more labile than the positions trans to ammonia ligand. *A chloride ion has a greater trans effect than ammonia.* Coordinating ligands have been arranged in a series of increasing trans effect:

$$H_2O < OH^- < NH_3 \sim RNH_2 < py < Cl^- < Br^- < NCS^- < I^- < NO_2^- \\ < PR_3 \sim SC(NH_2)_2 \sim CO \sim C_2H_4 \sim CN^-$$

The usefulness of the trans effect concept is shown in the synthesis of *trans* $[PtI_2(R_3P)_2]$ via reaction of K_2PtI_4 and R_3P:



Two major theories have been proposed to explain trans effect:

A. Polarisation Theory: When platinum (II) is bonded to a strongly polarising ligand at one of the four points of the square plane there develops some induced dipole in the metal ion. A δ^+ charge on platinum (II) faces the polarising ligand while a δ^-charge faces the ligand trans to the polarising ligand. This δ^- charge somewhat repels the trans ligand (Fig. 28.1).

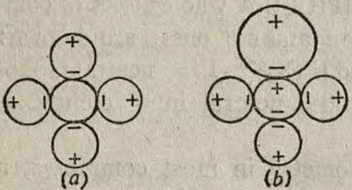


Fig. 28.1. Polarisation effects in square planar platinum (II) (*a*) platinum (II) is in an environment of four identical ligands (*b*) one of the ligands is more polarising-developing a trans effect

B. π-Bonding Theory: Kinetic studies on substitution reactions in square planar platinum (II) have now established that such reactions proceed via formation of an expanded coordination number. A five coordinate intermediate is first formed, which then dissociates to give the substituted complex and the knocked-off ligand

(Fig 28.2.). Any explanation of the trans effect must therefore take into account the facile approach of the incoming ligand and weakening of the bond trans to the trans-labilising ligand.

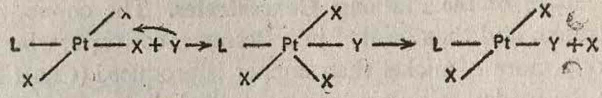


Fig. 28.2. Substitution reaction in Pt(II) complexes

It is noteworthy that the ligands with large trans effect are also those which are capable of forming π-bonds. Platinum (II) has the electronic configuration [Xe]$4f^{14}5d^8$. Square planar platinum (II) has four $5d\ 6s\ 6p^2$ hybrid sigma orbitals. These sigma orbitals overlap with filled sp^3 (eg: of PR_3) or sp (eg: of CO) lone pairs of the four ligands. The four remaining orbitals of platinum namely d_{xy}, d_{xz}, d_{yz} andd_{z^2} are filled. Taking the xy plane as the molecular plane it is clear that π-overlap of empty ligand orbitals (d_{xy} or d_{xz} of PR_3, Cl^- or the antibonding π*M.O. of CO) with filled d_{xz}, d_{xy} platinum (II) orbitals can occur. When a strong π-bond is formed (Fig. 28.3) a lowering of electron density between the metal ion and the ligand trans to the π-bonding takes place. This, in turn, facilitates the approach of the substituent in a direction trans to the trans labilising ligand. Such π-bonding hardly affects the electron density between the metal and the ligand *cis* to the trans labilising ligand.

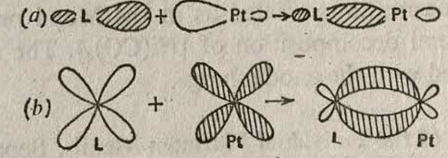


Fig. 28.3. Bonding between Pt(II) and π-bonding ligand L
(*a*) σ-bond (**d**) π-bond

28.10.5. Zerovalent Palladium and Platinum. It is remarkable that no carbonyl analogue of $Ni(CO)_4$ exists with palladium or platinum. But some other nickel analogues do exist. Thus corresponding to $[Ni(PF_3)_4]$ we have $[Pd(PF_3)_4]$ and $[Pt(PF_3)_4]$. These have been obtained by the action of PF_3 on $PdCl_2$ or $PtCl_2$ in presence of copper (as halogen acceptor) at 100°C.

28.11. ISOLATION OF THE PLATINUM METALS

Copper-nickel sulphide ores of the Sudbury district of Ontario State (Canada) has the highest amount of platinum metals ($\sim\frac{1}{2}$ppm.) Huge quantities of copper and nickel are extracted from the Sudbury ores so that the amount of the platinum metals extracted as by-product becomes commercially viable. The isolation of the platinum metals from this ore can be considered in two stages:

1. Isolation of the platinum concentrates 2. Isolation of the individual platinum metals.

28.11.1. Isolation of the Platinum Concentrates. The copper-nickel sulphide ore is concentrated, and then treated in a Bessemer converter whereby a Bessemer matte containing more of nickel than copper is produced (Chart 28-III). During this operation the oxidation by air is so controlled that some metallic nickel and copper are also produced. These free metals act as collectors of the precious metals, and the resulting alloy is separated by a magnetic separator. This alloy is next mixed with enough sulphur to convert most of the copper and nickel to their sulphides. The small amount of copper and nickel still remaining makes a concentrated alloy of the platinum metals and other precious metals (Ag, Au) and is again separated by a magnetic separator. This concentrated alloy is next subjected to electrolytic refining (with the alloy as anode) when the platinum metals are thrown down as anode sludge.

The copper-rich material obtained at the beginning (Chart 28-III) is worked by floatation process to get a separation of nickel concentrate and copper concentrate. The nickel concentrate is treated as in the Mond process thereby getting pure nickel via thermal decomposition of $[Ni(CO)_4]$. The residue left has $\sim 4\%$ Pt metals and is mixed with the anode sludge.

28.11.2. Isolation of the Individual Platinum Metals. Separation and isolation of the individual platinum metals are based on the differences in their behaviour towards acids or on the differences in solubility of their complexes. Some important differences are enumerated below:

(*a*) Hot aqua regia treatment converts Pt, Pd and Au into their soluble chloro complexes whereas Ru, Ag remain mostly as insoluble chloride. Rh and Ir remain unaffected by aqua regia.

(*b*) Reduction of the above chloro complexes by $FeSO_4$ precipitates gold metal and Pd(IV) is reduced to $[PdCl_4]^{2-}$.

$$3Fe^{2+} + AuCl_4^- \rightarrow 3Fe^{3+} + 4Cl^- + Au$$

$[PtCl_6]^{2-}$ remains unaffected by $FeSO_4$ and can be precipitated as the ammonium chloroplatinate $(NH_4)_2[PtCl_6]$ by the addition of NH_4Cl. The chloropalladate (II) is then treated with NH_4OH followed by HCl to precipitate the metal as $[Pd(NH_3)_2Cl_2]$.

(*c*) The insoluble residue from the aqua regia extraction is smelted with litharge (PbO), charcoal and Na_2CO_3. The resulting lead alloy is cupelled to reduce the lead content and the lead and silver dissolved by HNO_3.

(*d*) Ru, Rh, Ir and Os remain behind after HNO_3 treatment. Rhodium is now extracted by $KHSO_4$ fusion when it goes into solution as a sulphato complex. Rhodium (III) is now precipitated as $(NH_4)_3[Rh(NO_2)_6]$.

(*e*) The insoluble part remaining after $KHSO_4$ fusion is now fused with a mixture of KOH and KNO_3. Both Ru and Os go to solution as K_2RuO_4 and K_2OsO_4. Ruthenate can be reduced with HCl-alcohol but osmate remains unaffec-

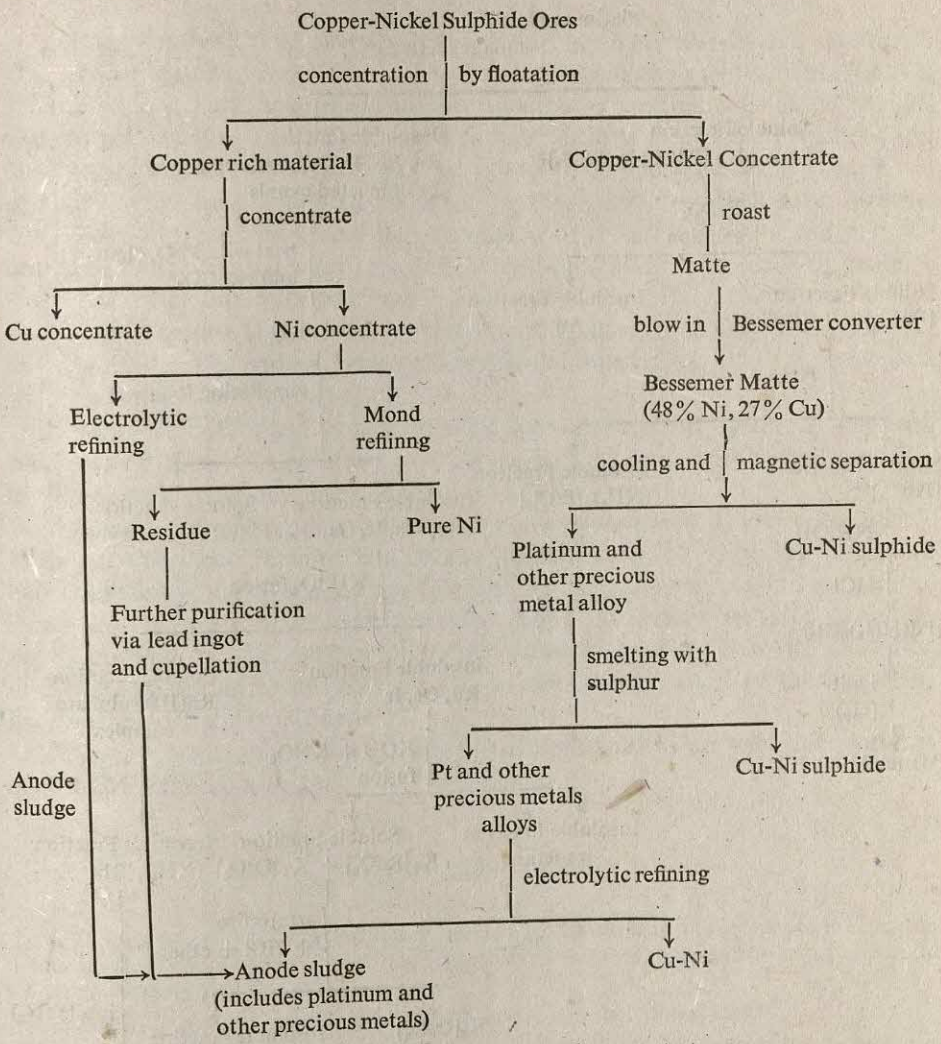

Copper-Nickel Sulphide Ores
concentration | by floatation
Copper rich material
Copper-Nickel Concentrate
concentrate
roast
Matte
Cu concentrate
Ni concentrate
blow in | Bessemer converter
Bessemer Matte
(48% Ni, 27% Cu)
Electrolytic refining
Mond refiinng
cooling and | magnetic separation
Residue
Pure Ni
Platinum and other precious metal alloy
Cu-Ni sulphide
Further purification via lead ingot and cupellation
smelting with sulphur
Anode sludge
Pt and other precious metals alloys
Cu-Ni sulphide
electrolytic refining
Anode sludge (includes platinum and other precious metals)
Cu-Ni

Chart 28-III. Platinum metals concentrates

ted. The osmate is precipitated as $(NH_4)_2[OsO_4]$. But iridium remains unaffected. The best solvent for iridium seems to be a mixture of conc. HCl and $NaClO_3$ at a temperature ~ 150°C.

Chart 28-IV describes the isolation of the individual platinum metals.

28.12. USES OF THE PLATINUM METALS

Platinum: Platinum is used in resistance thermometers and thermocouples. Because of low contact resistance platinum has a good demand for contacts in relays, alarm equipments etc. In the laboratory platinum is used in the form of crucibles, dishes, boats etc. Electrodes for conductance measurements and electro-

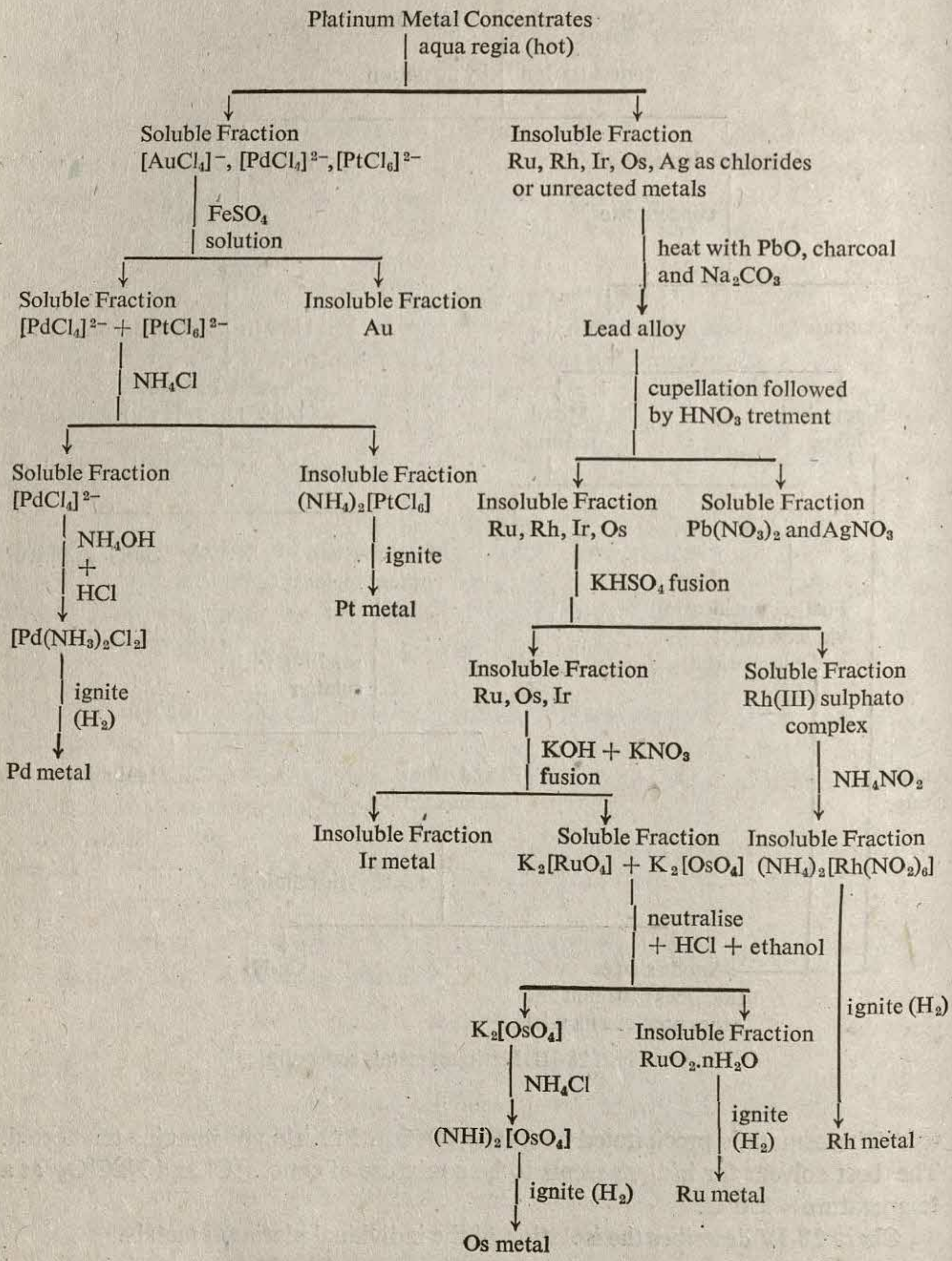


Chart 28-IV. Separation of individual platinum metals.

chemical analyses are also made of platinum. Considerable amount is also used in jewelry. Platinum metal has exceptional catalytic properties. It is used as a catalyst in the manufacture of H_2SO_4 by contact process (oxidation of SO_2 to SO_3) in the form of platinised asbestos. It is used as a platinum gauze catalyst in the oxidation of NH_3 to NO.

Platinised asbestos is asbestos impregnated with finely divided platinum. One technique to make platinised asbestos is to saturate the asbestos with H_2PtCl_6 solution. The mass is then made slightly alkaline by treating with dilute NaOH, and the platinichloride is then reduced to fine particles of platinum with sodium formate. The reduction is best done at 300-400°C. The asbestos is then freed of alkali by washing with water, and finally the material is dried in a furnace. Alternatively, the asbestos can be saturated with $(NH_4)_2PtCl_6$ and the material heated to incandescence when series of thermal decompositions occur to produce finely divided platinum on asbestos.

Platinum sponge is produced by prolonged ignition of $(NH_4)_2PtCl_6$ in a Pt dish at $\sim$600°C. The ignited sponge is boiled with dilute HCl and then with distilled water. It is then again ignited gently.

Platinum black is made by heating a 5% solution of H_2PtCl_6, neutralising with Na_2CO_3 and then pouring into a solution of sodium formate. The black residue is washed with water and dried over conc. H_2SO_4.

Palladium: An outstanding feature of metallic palladium is its ability to occlude hydrogen gas which remains in an active state. Because of its ability to adsorb and activate hydrogen it finds use as a catalyst in a number of industrial and laboratory scale hydrogenation reactions. Some important catalytic reactions are hydrogenation of acetylene to ethylene, production of H_2O_2 by the oxidation of 2-ethylanthraquinol and the reduction of the quinone back to the quinol by hydrogen on palladium (Chapter 19).

Palladium black and *palladised asbestos* are obtained as outlined for platinum black and platinised asbests.

STUDY QUESTIONS

1. Discuss the general characteristics of the Group VIII elements in the light of their atomic structures. How would you justify the three columns in this same group as has been done in the long from Periodic Table?

2. Briefly describe the metallurgy and applications of cobalt and nickel.

3. Iron, cobalt and nickel are typical transition elements. Justify the statement from a general resume of their properties.

4. Discuss the general requirements for stabilisation of high and low oxidation states of transition elements in relation to iron, cobalt and nickel.

5. Discuss the different hybridisation schemes (valence bond theory) and also crystal field theory with respect to typical compounds of iron, cobalt and nickel in the oxidation states + 2, + 3 and + 4.

6. Write notes on: (*a*) hexavalent iron (*b*) quadrivalent nickel (*c*) univalent cobalt (*d*) zero-valent iron, cobalt and nickel.

7. Give the preparation and properties of (*a*) potassium ferrate (*b*) potassium ferrocyanide (*c*) cobaltic alum (*d*) Mohr's salt (*e*) hexamminecobalt(III) chloride (*f*) sodium nitroprusside (*g*) nickel tetracarbonyl.

8. Give an outline of the extraction of the platinum metals from Sudbury nickel ores.

9. Compare and contrast the chemistry of nickel with the chemistries of palladium and platinum.

10. What is the difference between pig iron and steel? Name some important alloy steels and mention their uses.

11. Describe briefly the Bessemer and the open hearth process for making steel. Discuss their merits and demerits.

12. Discuss the role of complex formation in the detection and estimation of transition metals with respect to iron, cobalt and nickel.

13. Explain why palladium (II) and platinum (II) complexes are so readily spin-paired while this is not the case with nickel (II) complexes.

14. What is trans effect? How does this concept help in the syntheses of many cis and trans isomers of platinum (II) complexes? How would you proceed to offer an explanation of this effect?

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29

Group IB
Copper, Silver and Gold

Copper, silver and gold constitute the family of coinage or currency metals. These are noble metals and often occur native in nature. Their relative abundances are: copper ($7 \times 10^{-3}\%$); silver ($2 \times 10^{-5}\%$) and gold ($5 \times 10^{-7}\%$).

29.1. COMPARATIVE STUDY OF THE GROUP IB ELEMENTS

29.1.1. General Considerations. In the Mendeleev classification copper, silver and gold are included alongwith the alkali metals in two subgroups of Group I. The resemblances of the two subgroups do not extend beyond their having one electron in the outermost orbital. The long-form Periodic Table largely removes this deficiency of classification by putting the two subgroups IA and IB in widely separated columns. Although these elements in their atomic states have a filled *d* subshell (Table 29.1) they are considered as transition elements because their + 2 and + 3 states do possess incompletely filled *d*-subshell. Typical of transition elements the currency metals also exhibit variable valences. The valences exhibited are:

Copper	+ 3	+ 2	+ 1
Silver	+ 3	+ 2	+ 1
Gold	+ 3	...	+ 1

Note in particular that the alkalies being non-transition elements show one valence only, namely + 1. Both the alkalies and the currency metals have filled inner orbitals but the alkalies have a noble gas core whereas the currency metals a pseudo-noble gas core. The *d*-orbitals are not efficient in shielding the *s* electrons from the nuclear charge. This makes the first ionisation potential of the currency metals comparatively higher (I.P. Na 5.14 *ev*; Cu, 7.72 *ev*). That the noble gas core is more stable than pseudo noble gas core is shown by the second ionisation potential of sodium being larger than that of copper (Na, 41.07 *ev*; Cu, 20.29 *ev*). Fajans' rules say that the currency metals with pseudo-noble gas cores are more liable to deformation and hence they are likely to give covalent or complex compounds much more readily than the alkalies.

Table 29.1. Electronic Configurations and Some Properties of Group IB Elements

Element	Atomic Number	Electronic Configuration	Ionisation Potential (*ev*)	Electro-negativity
Copper	29	$[Ar]3d^{10}4s^1$	7.22, 20.29, 36.83	1.9
Silver	47	$[Kr]4d^{10}5s^1$	7.57, 21.48, 34.82	1.9
Gold	79	$[Xe]4f^{14}5d^{10}6s^1$	9.22, 20.5...	2.4

A consequence of both the alkalies and the currency metals having one electron in the outermost *s*-orbital is a common $+1$ oxidation state. The resemblance between these two subgroups extends only to the numerical value of the common oxidation state and goes no further. The cuprous, argentous and the aurous compounds have a strong tendency to assume covalent state, the tendency increasing from cuprous to aurous. On the other hand the alkalies exhibit chemistries typical ef strong monovalent cations (Chapter 14). In the $+2$ and $+3$ states these IB elements behave as typical transition elements giving coloured compounds, some having paramagnetic properties. Their higher oxidation states are stabilised in complex compounds. Some of the variations in properties within the subgroup are not however easily explained. In the earlier transition groups we have observed a general trend that higher oxidation states are more stable with the heavier elements. With gold $+3$ state is the stablest and commonest but with silver the $+1$ state is the stablest and commonest whereas with copper $+2$ state is the stablest. The $+2$ state in gold is little known. The monovalent ions are soft acids, the bivalent and the trivalent ions are borderline or hard acids. Thus Cu^+ forms stable complexes with soft donors. The standard potential (Table 29.2) of $M^+ + e \rightleftharpoons M$ couple becomes more positive from copper through silver to gold. This trend is opposite to what we find with the

Table 29.2. Some More Properties of Group IB Elements

Element	Atomic Radius(A)	Ionic (M^+) Radius (A)	M.P. (°C)	B.P. (°C)	Density (gm/ml)	$E°$ (volts) $M^+ + e \rightleftharpoons M$
Copper	1.28	0.96	1083	2595	8.9	+0.52
Silver	1.43	1.26	960	2212	10.5	+ 0.79
Gold	1.44	1.37	1063	2966	19.3	+ 1.68

alkalies, the general group trend being increasing electropositive character with increasing atomic number. The standard potentials thus indicate the difficulty of the metals to pass into the + 1 state, and therefore points to the increasing noble character from copper to gold.

Silver and gold are of similar atomic radii although their atomic weights are substantially different (Ag, 107.87; Au, 196.97). Hence their densities show an almost two-fold increase from 10.5 (Ag) to 19.3 (Au) (Table 29.2).

29.1.2. Chemical Behaviour. *Hydrides:* Of the three elements copper alone forms a hydride of almost a definite composition CuH, obtained by the action of H_3PO_2 on warm copper sulphate solution. The hydride is insoluble, cannot be purified and readily loses hydrogen on warming. In oxygen it forms CuO and H_2O. Silver and gold absorb hydrogen at elevated temperatures but give no compounds of definite composition

Oxides: Cuprous oxide is obtained as a yellow powder obtained by careful reduction of an alkaline solution of copper (II) salts with hydrazine, or as red crystals by the thermal decomposition of CuO.

Argentous oxide separates in black or brown crystals on the addition of alkali to a solution of silver (I) salt. The oxide is mostly basic since it produces with acids silver (I) salts. The oxide absorbs CO_2 from the air. It however has a small tendency to show acid properties since it is more soluble in alkalies than in pure water.

Aurous oxide Au_2O can be made by treating potassium aurobromide, $KAuBr_2$, with alkali. Like Ag_2O it is somewhat amphoteric.

Cupric hydroxide, obtained as a blue green precipitate on the addition of alkali to a cupric solution, is to some extent amphoteric. When freshly precipitated, it is slightly soluble in alkali giving a violet solution $M_2[CuO_2]$ or $M_2[Cu(OH)_4]$ It is however more basic than acidic since it readily reacts with acids to give cupric solution.

Black argentic oxide, AgO, (in reality $Ag_2O_3 + Ag_2O$) obtained by oxidising silver (I) salts with $K_2S_2O_8$, NaOCl or electrolytically, is mostly basic as it dissolves in acids to give some Ag^{2+} in solution.

An auric solution reacts with magnesia to precipitate magnesium aurate $Mg[AuO_2]_2$. which on treatment with acid gives AuO.OH. This is a weak acidic oxide dissolving in aqueous KOH to give $KAuO_2$ or $K[Au(OH)_4]$.

Cu_2O_3 has been obtained by the oxidation of a solution of a sodium cuprite Na_2CuO_2 by NaOOH. It is a red powder which is decomposed by acids to copper (II) and oxygen but dissolves slightly in alkalies.

On the whole + 3 oxides are mostly acidic, + 2 oxides are amphoteric and the + 1 oxides are mostly basic. This must be noted however that the basic nature of the +1 oxides is rather poor, and stands nowhere near the very strongly basic alkali metal oxides.

Halides: The cuprous halides are generally obtained by the reduction of cupric halides by copper. The solubility of the cuprous halides in water decreases from the chloride to the iodide. They are poor conductors and polymerised even in the vapour state (being dimeric and trimeric). The insolubility of silver halides (with the exception of AgF) in polar solvents and their weak electrolytic behaviour also point to considerable covalent character. Notably AgF is quite soluble in polar solvents, behaves as a good electrolyte and has an ionic crystal structure. The best known gold (I) halide, the iodide, is covalent.

Cupric fluoride obtained from fluorine and copper is an ionic compound. The other anhydrous halides form layers of infinite halogen-bridged chains such that each copper (II) of a particular layer is coordinated to four halogens of that layer, and has two other halogens, from two other chains above and below, completing a coordination number six. Cupric halides are readily soluble in water forming the aquo cupric ions. Of the halides of silver (II) only AgF_2 is known. The chloride and the bromide of gold (III) are dimeric in the solid and vapour state, which is an evidence of their covalent nature.

Complexes: The three elements have a great tendency to form complex compounds. The + 1 state forms complexes with both π-bonding and non-π-bonding ligands. The higher oxidation states, following Fajans' rules, will be even more complexing. The + 3 state being very oxidising and very uncommon, complexation by suitable ligands is the only way of stabilising this valence.

The unipositive state of copper is stablised by soft donors like PR_3, olefines, acetylenes, cyanides etc. Silver (I) also forms complexes with NH_3, R_3P, acetylene etc. Complexes of gold (I) with similar ligands are also known.

Complexation of bivalent copper has been extensively studied. The element can assume coordination numbers 4, 5 and 6, and has a great tendency to assume distorted stereochemistries. The ion being a somewhat hard acid a very wide array of complexes with N, O, and halogen donors in tetrahedral, square planar, trigonal bipyramidal, square pyramidal and also octahedral geometry are known. Bivalent silver complexes with N and O donors with square planar and octahedral geometries are known.

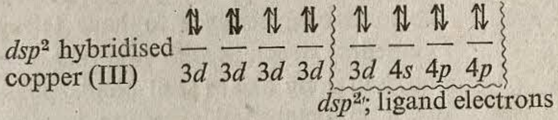
Copper (III) and silver (III) form similar square planar complexes with N and O donors. Gold (III) also tends to form square planar complexes with halogen donor and nitrogen donor ligands. A few five-coordinate and six-coordinate complexes have also been obtained.

Unipositive currency metal complexes are all diamagnetic (d^{10} system), bipositive complexes are paramagnetic (d^9 system; μ, 1.7 B.M.) and the tripositive complexes (d^8 system) are diamagnetic in square planar environment but paramagnetic ($\sim \mu$, 2.8 B.M.) in octahedral coordination.

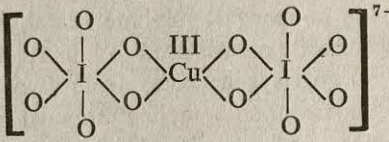
29.2. OXIDATION STATES OF COPPER

29.2.1. Trivalent Copper. Copper (III), a d^8 system, has been stabilised in a limited number of complexes. The hexafluoro copper (III) has been obtained as a pale green compound $K_3[CuF_6]$ by the action of fluorine on a mixture of KCl and $CuCl_2$ at 275°C. The substance is paramagnetic ($\mu = 2.8$ B.M.) indicating two unpaired spins in two of the five 3*d*-orbitals. On the crystal field model we assume that six electrons remain paired in the lower t_{2g} orbitals and two remain unpaired in the upper e_g level. More recently a series of hexafluoro cuprates (III) $M_3[CuF_6]$ (M = Na, K, Rb, Cs), $M_2M'[CuF_6]$ (M = K, Rb, Cs; M′ = Li, Na, K, Rb, Cs) have been obtained by fluorination (under high pressure) of appropriate chlorocuprate (II) or alkali halide/copper (II) chloride mixture. All are green microcrystalline solids and are paramagnetic ($\mu \simeq 2.9$ to 3.0 B.M.) indicating $3d^8$ copper (III) complexes in octahedral stereochemistry.

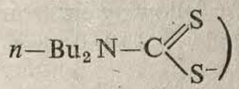
Following our general ideas on the stabilisation of high oxidation states tellurate and periodate groups (with tellurium and iodine in their highest oxidation states) have been found to stabilise copper (III). Anodic oxidation or peroxy-sulphate oxidation of an alkaline solution of bivalent copper in the presence of excess periodate gives red coloured diamagnetic crystals eg: $K_7[Cu(IO_6)_2]7H_2O$, $Na_7[Cu(IO)_6)_2]12H_2O$ etc. Diamagnetism results from a square planar ($Cu^{III}O_4$) coordination with dsp^2 hybridisation of the metal ion.



Structure (29-I) is thus suggested:


(29-I)

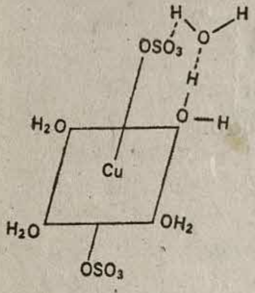
On the crystal field model square planar geometry splits the five *d*-orbitals (Fig. 10.15) in four sets: (d_{zx}, d_{yz}), (d_{z^2}), (d_{xy}) and $(d_{x^2-y^2})$. The energy difference between d_{xy} and $d_{x^2-y^2}$ is sufficient to cause spin pairing in the lower energy orbital (d_{xy}). Anodic oxidation of copper in strongly alkaline solution of potassium tellurate K_6TeO_6 or oxidation of copper (II) in strongly alkaline tellurate medium by $K_2S_2O_8$ gives maroon coloured compounds of copper (III), eg: $Na_7H_2[Cu\ (TeO_6)_2]12H_2O$. These compounds are also diamagnetic.

Violet coloured $[CuBr_2(n{-}Bu_2dtc)]$ (n-Bu_2dtc = n-butyldithiocarbamate =  has been prepared by bromine oxidation of $[Cu^I(n{-}Bu_2\ dtc)]$ in CS_2. As expected of a true copper (III) complex the Cu–Br(2.31A) and Cu–S (2.19A) distances are considerably shorter than those found in parallel copper (II) complexes (2.46A; 2.30A). The complex is diamagnetic as is expected for a square planar $3d^8$ complex.

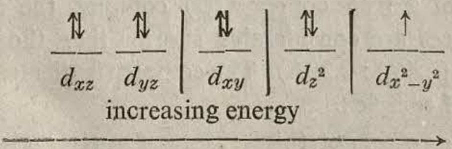
Copper (III) complex of biuret, (biH$_2$; $NH_2{-}\underset{\underset{O}{\|}}{C}{-}NH{-}\underset{\underset{O}{\|}}{C}{-}NH_2$), K $[Cu(bi)_2]$ was prepared as a brown solid by persulphate oxidation of $K_2[Cu(bi)_2]$ in 5*N* KOH solution. The complex reacted with acidified KI to liberate two equivalents of iodine per mole of the complex. The two end nitrogens of biuret lose one hydrogen each and get coordinated to copper (III) in a square planar array.

Copper (III) complexes of schiff bases of the type $[Cu(SB)(H_2O)_2]ClO_4$ (SBH_2 = ethylene bis (salicylaldimine) and related ligands) have been prepared as red brown solid by air/H_2O_2 oxidation of the copper (II) complexes in ethanol solution. The complexes are all paramagnetic (μ = 2.85—3.02 B.M.) as expected for $3d^8$ complexes in octahedral geometry.

29.2.2. Bivalent Copper. It has a rich coordination chemistry since it can give rise to several stereochemistries: tetrahedral with weak-field ligands eg: $[CuCl_4]^{2-}$, square planar with strong donors eg: $[Cu(BigH)_2[^{2+}$, square pyramidal eg: $[Cu(L)(acac)_2]$ L = pyridine, acacH = acetylacetone), trigonal bipyramidal eg: $[Cu(dipy)_2I]I$. Finally it is a common experience to have tetragonally distorted octahedral structure with four short equatorial bonds and two long axial (1, 6) bonds. The desire to assume distorted octahedral structure is also revealed in the dimerisation and polymerisation that many outwardly simple compounds of copper (II) undergo. For example, in copper (II) sulphate pentahydrate each copper (II) is directly coordinated to four H_2O molecules equatorially. Two oxygen atoms from two sulphate groups in the lattice then complete the axial coordination to copper. The fifth water molecule is hydrogen bonded between a sulphate group and a coordinated water molecule as shown in (29-II). The coordinated water molecules can be removed at 150—200°C. The removal of the fifth water molecule, which is different in kind from the others, often occurs with decomposition of the sulphate anion. Copper (II) acetate is dimerised in both solid state and in solution: $[Cu_2(CH_3COO)_4]2H_2O$. Each copper (II) is coordinated in a square plane by four oxygens of the bridging acetato groups. The two water molecules are bound one each to copper (II). Finally the copper—copper distance being short, the sixth coordination position of one copper is taken up by the second copper (29-III). This structure allows for a lateral overlap of the $d_{x}{}^{2}-{}_{y}{}^{2}$ orbitals of the two copper (II) ions. In crystal field model we assume the following electron distribution of the copper (II) ion in a tetragonally distorted octahedral complex (cf. Fig. 10-15):



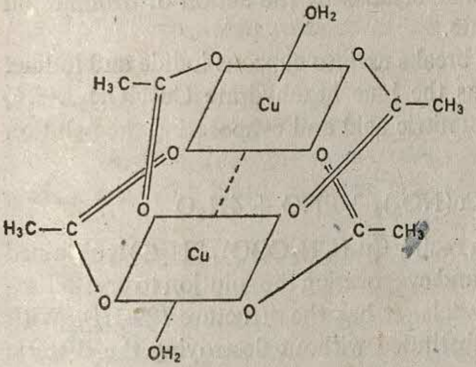
(29-II)



When the two copper (II) come close, as in the acetate, there is a scope for lateral overlap of the $d_{x^2-y^2}$ orbitals (Fig. 29-1).

Such a bond is called a δ-bond and is different from a σ-bond and a π-bond. Such overlap leads to a partial quenching of the magnetic moment in copper acetate

($\mu = 1.43$ B.M.). Many copper (II) complexes of tridentate dibasic schiff bases (SBH_2; donor set, ONO) [Cu(SB)] are really dimeric with the schiff base oxygen serving as bridges between two square planes. In such cases also low paramagnetic values are obtained due to exchange phenomena through the bridging oxygen atoms.



(29-III)

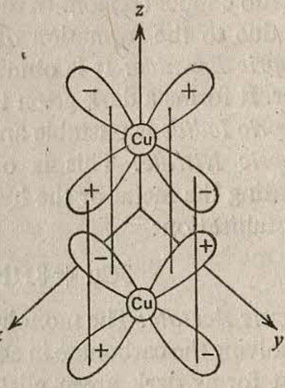


Fig. 29.1. Schematic representation of the formation of a δ-bond between $3d_{x^2-y^2}$ orbitals in copper (II) acetate

In aqueous medium all cupric salts are present as $[Cu(H_2O)_6]^{2+}$ ions. Addition of other ligands leads to successive replacement of these coordinated water molecules. With ammonia replacement in aqueous medium leads to $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (commonly written as $[Cu(NH_3)_4]^{2+}$). In liquid ammonia the hexammine is formed.

A variety of mixed ligand complexes have recently been synthesised eg: [Cu(dipy) (BigH)] X_2(X = halogen), [Cu(o-phen) (BigH)]X_2, [Cu(gly) (BigH)]X, [Cu(dipy) (SB)], [Cu(o-phen) (SB)] (SBH_2 = tridentate, dibasic schiff base O—N—O donors). All these complexes are believed to assume distorted octahedral structures particularly in coordinating solvents like water, pyridine.

Cupric Sulphate: This is obtained on a large scale by dissolving copper scrap in hot dilute sulphuric acid in the presence of air:

$$2Cu + 2H_2SO_4 + O_2 \rightarrow 2CuSO_4 + 2H_2O$$

Copper scrap is packed in a lead lined tower into which dilute H_2SO_4 is sprayed from the top and air and steam injected through the bottom. The copper sulphate solution collecting at the bottom is pumped to the top and sprayed over the scrap till a concentrated solution is obtained. It crystallises as the pentahydrate $CuSO_4 \cdot 5H_2O$. It is commonly called as blue vitriol, although like the true vitriols it does not crystallise with $7H_2O$. The pentahydrate loses four coordinated water molecules at 150—250°C changing to a very pale blue colour. This colour change is due to the positions of coordinated H_2O groups being taken up by sulphato oxygen which are weaker ligands. Therefore the *d—d* transitions occur at much lower energy (close to the infrared region). On strong heating the pentahydrate decomposes to CuO. Copper sulphate is used in copper plating, as a mordant in dyeing, as a germicide and as a green pigment.

Cupric Chloride: The anhydrous chloride is obtained by heating copper in a stream of chlorine. From aqueous medium it crystallises as the dihydrate. The dihydrate can also be obtained by treating copper hydroxide or the carbonate with aqueous HCl. Dilute aqueous solution is blue, which is the colour of the hexaaquo copper (II) ion. In the presence of large excess of Cl^- ions it looks yellow green due to the formation of the tetrahedral tetrachlorocuprate (II) ion.

Cupric Bromide: It is obtained as black crystals by the action of bromine on copper. It forms a dark green tetrahydrate.

Cupric Iodide is unstable and readily breaks up into cuprous iodide and iodine.

Cupric Nitrate: This is obtained as the blue hexahydrate $Cu(NO_3)_2.6H_2O$ by treating the metal or the hydroxide in nitric acid and evaporating the solution to crystallisation:

$$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

Cupric Acetate: The monohydrate (in reality $Cu_2(CH_3COO)_4.2H_2O$) is obtained by dissolving the carbonate in acetic acid and evaporating the solution to crystallisation. It forms dark green glistening crystals. It has the structure (29-III). With pyridine the two H_2O molecules are substituted without destroying the dimeric structure.

A basic acetate $(CH_3COO)CuOH$, called *verdigris*, is a green pigment. It is obtained by exposing copper plates to the action of acetic acid in the presence of air:

$$Cu + CH_3COOH + \tfrac{1}{2}O_2 \rightarrow (CH_3COO)CuOH$$

Electronic Spectra: Fig 11.10 tells us that $3d^9$ copper (II) has a ^2D Russell Saunders term which splits into a ^2E_g ground state and a $^2T_{2g}$ excited state so that in an octahedral field a single spin-allowed but Laporte forbidden transition $^2E_g \rightarrow {}^2T_{2g}$ is possible. But this ion is very sensitive to Jahn-Teller distortion and hence very rarely any undistorted stereochemistry is observed. Due to distortion $^2T_{2g}$ splits into ^2E_g and $^2A_{1g}$ while the ^2E_g splits into ^2B_g and ^2A_g so that a cluster of bands is likely. In terms of orbitals we may have the transitions: $d_{z^2} \rightarrow d_{x^2-y^2}$; $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xz} \rightarrow d_{x^2-y^2}$. In terms of positron holes these electron transitions will be reversed. Usually all pseudo octahedral copper (II) complexes are characterised by a broad asymmetric band around $16kK$. Regular tetrahedral complexes are also uncommon due to the splitting of the $^2T_2$ ground state by JahnTeller effect.

29.2.3. Monovalent Copper. Cuprous copper has a strong tendency to disproportionate into metallic copper and cupric copper (Chapter 27). Taking the very minute solubility of metallic copper as constant we can write the following equilibrium constant for the disproportionation reaction:

$$2Cu^+ \rightleftharpoons Cu + Cu^{2+}\,;\ K = \frac{[Cu]\,[Cu^{2+}]}{[Cu^+]^2}\ ;\ K = \frac{[Cu^{2+}]}{[Cu^+]^2}$$

The equilibrium constant has a value 1×10^6. Therefore in a molar solution of Cu^{2+} the equilibrium concentration of $[Cu^+]$ can be no more than $10^{-3}\ M$. Thus

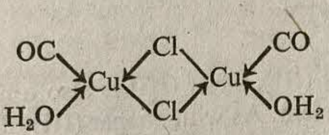
Cu^+ ion will readily disproportionate to attain the K value. Hence cuprous copper can only survive in appreciable quantity in solution only if it is forced not to ionise in solution. The oxide, sulphide and the halides (with the exception of the fluoride) can be prepared because they are so insoluble that the above equilibrium cuprous concentration is not attained. Most other cuprous compounds known are in the form of complexes so that the above equilibrium need not be considered.

The equilibrium of the reaction $2Ag^+ \rightleftharpoons Ag^{2+} + Ag$ is very much to the left. The Ag^{2+} has a strong tendency to act as an oxidant and revert to the Ag^+ state. This oxidation state is therefore obtained only when protected through complexation.

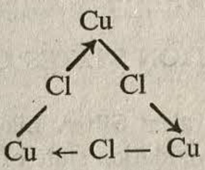
The behaviour of gold is more like copper and the disproportionation reaction $3Au^+ \rightleftharpoons Au^{3+} + 2Au$ proceeds readily from left to right. The complexation tendency of Au^{3+} being large makes evaluation of the equilibrium constant rather difficult.

Cuprous Oxide: This is obtained by the reduction of CuO by copper or by thermal decomposition of CuO. Cuprous oxide is also prepared as a red precipitate by reducing a cupric salt in alkaline solution with glucose. The oxide is soluble in ammonia to give the complex $[Cu(NH_3)_2]^+$ ion. With KCN, the complex compounds $K_3[Cu(CN)_4]$, $K_2[Cu(CN)_3]$ and $K[Cu(CN)_2]$ are formed. The tetracyano complex is the major species.

Cuprous Halides: Cuprous chloride is commonly prepared by heating cupric chloride, copper turnings and concentrated HCl on a steam bath until the green colour of Cu^{2+} disappears. The solution is then dropped into an aqueous solution of SO_2(serving as a reducing medium) when cuprous chloride separates as a white precipitate. This is collected, washed with aqueous SO_2, alcohol and ether. Cuprous chloride dissolves in ammonia forming a dark green solution containing $[Cu(NH_3)_2]OH$. This solution can absorb CO forming CuCl.CO. Carbon monoxide absorption also occurs when CuCl is dissolved in bases such as pyridine, aniline, etc. From these solutions colourless crystals of a halogen-bridged dimer $[CuCOCl]_2.\,2H_2O$ (29-IV) are obtained:



(29-IV)



(29-V)

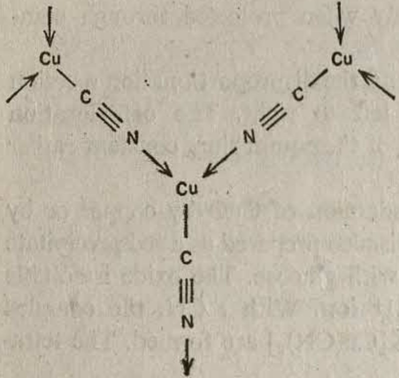
Cuprous chloride is a cyclic trimer (29-V) in the vapour state with alternating chlorine and cuprous atoms. In the solid state it has four chloride ions tetrahedrally disposed about it (cf: zinc blende structure; Part I) The *cuprous bromide* is obtained as a pale yellow insoluble product by reducing cupric bromide by excess copper as is done for CuCl. Its properties are comparable to those of CuCl. *Cuprous iodide* is readily obtained by the addition of KI to a cupric solution:

$$Cu^{2+} + 2I^- \rightleftharpoons CuI + \tfrac{1}{2}I_2$$

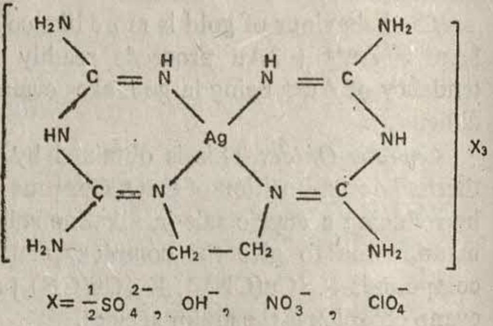
Unlike the chloride and the bromide it is not oxidised in air.

Cuprous Acetate: This has recently been obtained as pale yellow plates by the reduction of cupric acetate in pyridine or acetonitrile by finely divided copper. The structure consists of infinite planar chains of binuclear dimeric units, $[Cu(Ac)]_2$, which are bridged through copper and oxygen atoms to form a polymer. Each copper is bonded to three oxygen atoms and another copper atom in a distorted square planar configuration.

Cuprous Complexes: Cuprous complexes show varying coordination numbers. When the coordination number is 2 the structure is linear, with coordination number 4 the stereochemistry is tetrahedral and in a few cases a planar coordination of three unidentate ligands is known. Typical examples are $[Cu(NH_3)_2]^+$, $K_3[Cu(CN)_4]$, $K_2[Cu(CN)_3]$, $K[Cu(CN)_2]$ etc. In $K[Cu(CN)_2]$ the metal does not obey the apparent coordination number two; instead the compound has a spiral structure (29-VI) such that copper (I) has a coordination number three.



(29-VI)



(29-VII)

Stable complexes of cuprous iodide with substituted phosphines, arsines and sulphides have been synthesised eg: $[(R_3P)_2Cu]ClO_4$, $[R_3P.CuI..dipy]$, $[Cu\{SC(NH_2)_2\}]X$ etc.

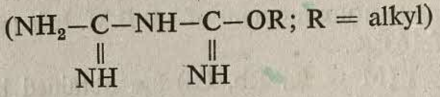
29.3. OXIDATION STATES OF SILVER

29.3.1. Trivalent Silver. Like copper (III), silver (III) is also a d^8 system and is an unusual oxidation state of the element. As with copper (III), fluorine reacts with a mixture of KF and AgF on heating to produce yellow $KAgF_4$. With CsF the complex $CsAgF_4$ is obtained. The fluoro complexes are diamagnetic. A square planar stetreochemistry with dsp^2 hybridisation or a crystal field splitting of the type (d^2_{xz}, d^2_{yz}), $(d^2_{z^2})$, (d^2_{xy}) $(d^0_{x^2-y^2})$ is suggested. The complex is very sensitive to moisture. Stabilisation of silver (III) has also been achieved by periodate and tellurate groups. Peroxydisulphate oxidation of strongly basic solutions containing TeO_6^{6-} or IO_6^{5-} and Ag^+ gives dark red diamagnetic complexes: $K_6H[Ag(IO_6)_2]10H_2O$, $Na_6H_3[Ag(TeO_6)_2]18H_2O$ etc. Their structures and hybridisation schemes are comparable to those of copper (III).

A series of very stable cationic silver (III) complexes with the quadridentate ethylenedibiguanide ligand ($Et(BigH)_2$) has been prepared. The complex sulphate is obtained as a dark orange substance by potassium peroxydisulphate oxidation of a solution containing silver sulphate and ethylenedibiguanide sulphate. The base is violet, and produces on neutralisation with $HClO_4$ or nitric acid the complex perchlorate or nitrate salt. The nitrate salt is remarkably stable and can be recrystallised from hot dilute nitric acid solution. The complex (29-VII) $[AgEt(BigH)_2]X_3$ is square planar since it is diamagnetic. An X-ray crystal structure study shows a primary square coordination around Ag (III) and a coordination of one or two counter anions at a significantly longer distance. The molar conductance of the salts in aqueous solution is comparable to those of other triunivalent electrolytes. These are all strong oxidants and liberate two equivalents of iodine from acidified iodide solution.

Silver (III) complexes of biguanide has also been recently reported as brown silky crystals: $[Ag(BigH)_2](OH)SO_4$.

Silver (III) complexes of 1-amidino–O–alkylurea (AAUH)



$$(NH_2-\underset{\underset{NH}{\|}}{C}-NH-\underset{\underset{NH}{\|}}{C}-OR;\ R = \text{alkyl})$$

have also been isolated as red/orange crystals $[Ag(AAU)_2]\ X(X = OH^-;\ \frac{1}{2}SO_4^{2-})$. These are diamagnetic. These complexes behave as two-electron oxidising agents towards ferrous sulphate or acidified potassium iodide. A square planar configuration is indicated. A silver (III) complex of biuret (cf: 29.2.1) $[Ag(biH_2)_2]\ (NO_3)_3$ has been prepared by persulphate oxidation of a silver (I) complex followed by precipitation with sodium nitrate. Square planar $Ag^{III}N_4$ has been proposed.

Silver (III) complex of o-phenylenebisdimethylorsine $[Ag\,(diars)_2]\ (ClO_4)_3$ has been obtained as yellow solid by conc. HNO_3 oxidation of the silver (I) complex $[Ag\,(diars)_2]ClO_4$ in $HClO_4$.

29.3.2. Bivalent Silver. The compounds of silver (II) may be classified under simple compounds and complexes. Two simple compounds, argentic oxide and argentic fluoride are known. The complexes are either non-electrolytes or cations and the predominant coordination number is four.

Several methods are available for the synthesis of argentic oxide: (1) Peroxydisulphate oxidation of silver nitrate gives a greyish black precipitate $Ag_7O_8NO_3$ which decomposes in boiling water to give AgO:

$$Ag_7O_8NO_3 \rightarrow 6AgO + AgNO_3 + O_2$$

(2) Oxidation of silver nitrate by $K_2S_2O_8$ in an alkaline medium also gives AgO:

$$4AgNO_3 + 2K_2S_2O_8 + 8NaOH \rightarrow 4AgO + K_2SO_4 + 3Na_2SO_4 + 2NaNO_3 + 2KNO_3 + 4H_2O$$

(3) Electrolytic oxidation of silver nitrate solution gives at the anode $Ag_7O_8NO_3$ which can be decomposed by boiling water to give AgO. (4) Ag_2O can be oxidised to AgO by NaOCl in alkaline medium. AgO is not a peroxide, Ag_2O_2, since no

H_2O_2 is formed on acidification. Oxidimetric titration indicates an overall +2 state for silver. Interestingly the substance is diamagnetic. +2 silver with a d^9 configuration should be paramagnetic. A structural study has shown that the crystal lattice contains two kinds of silver—silver (III) and silver (I). Thus AgO is really a mixed valence compound $Ag^IAg^{III}(O^{2-})_2$. This formulation will explain the average oxidation number as also the diamagnetism. Ag^I is a d^{10} system and Ag^{III} in square planar coordination with oxide ions will also be diamagnetic. The compound is a strong oxidant, oxidising iodide to iodine, ferrous to ferric, thiosulphate to trithionate and sulphate etc.

The only other simple compound is AgF_2. This is obtained by reacting silver or silver (I) fluoride with fluorine at ~400°C. It is a dark brown substance which reacts with water liberating oxygen and ozone. It is a powerful oxidant which oxidises ethanol to acetaldehyde, chromium (III) to chromate, manganese (II) to permanganate etc. It is also a powerful fluorinating agent converting SO_2 and CO_2 to SO_2F_2 and COF_2 respectively. CCl_4 is converted to CF_4. It is paramagnetic with a room temperature moment of 2.0 B.M. It is antiferromagnetic with a Neel temperature of 163°K.

Blue M_2AgF_4 (M = K, Rb, Cs) are obtained by heating appropriate proportions of MF and AgF_2 under argon. The compounds have magnetic moments in the range 1.5—1.7 B.M.

Suitable ligands for the purpose of stabilisation of silver (II) are pyridine, dipyridyl, o-phenanthroline, picolinic acid and other pyridine carboxylic acids. Addition of aqueous $K_2S_2O_8$ to an aqueous pyridine solution of silver (I) sulphate gives orange crystals of $[Ag(py)_4]S_2O_8$. Complexes $[Ag(dipy)_2]^{2+}$, $[Ag(o\text{-}phen)_2]^{2+}$ are also similarly obtained. With terpyridyl (terpy), complexes of the type [Ag(terpy) X]X (X = ClO_3^-, ClO_4^-, NO_3^-) have been isolated. These compounds are all orange to red. These are good oxidants, and are paramagnetic ($\mu \sim 1.8$ B.M.). The complexes are believed to possess square planar stereochemistry with one spin as shown below:

$$\text{Valence Bond:}\quad \begin{array}{cccc|cccc|c} \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow \\ \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} & \text{—} \\ 4d & 4d & 4d & 4d & 4d & 5s & 5p & 5p & 5p \end{array}$$

$$\underbrace{\qquad\qquad\qquad}_{dsp^2;\ \text{ligand electrons}}$$

$$\text{Crystal Field:}\quad d^2_{xz},\ d^2_{yz} \mid d^2_{z^2} \mid d^2_{xy} \mid d^1_{x^2-y^2}$$

increasing energyy

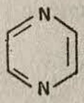
$$\xrightarrow{\qquad\qquad\qquad\qquad}$$

Using an excess of terpyridyl a brown coloured $[Ag(terpy)_2]S_2O_8$ has been obtained via persulphate oxidation of silver(I). Pyridine mono-, di- and tricarboxylic acids have also been extensively studied. Peroxydisulphate oxidation of silver (I) in aqueous picolinic acid gives the insoluble square planar bis(picolinato)silver(II). Similar bis-ligand complexes have also been reported with nicotinic acid and isonicotinic acid. The structures of these latter complexes are believed to be either dimeric or polymeric. With pyridine 2, 6-dicarboxylic acid ($LutH_2$) a complex

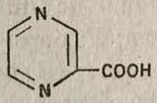
$[Ag(Lut)(LutH_2)].H_2O$ (dark brown) has been reported, in which silver (II) is six coordinate.

Several mixed ligand complexes containing pyridinic 2, 6 dicarboxylic acid and terpyridyl, bipyridyl or ortho-phenan-theroline (L) have been prepared. These Complexes [Ag (Lut) (L)] XH_2O have normal one electron moment.

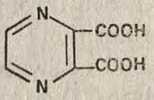
This area has recently been enriched. Pyrazine (29-VIII), pyrazine-2-carboxylic acid (29-IX) and pyrazine-2, 3-dicarboxylic acid (29-X) have been found to stabilise silver (II). As the pyrazine moiety has two nitrogens at 1, 4 positions, and is capable or functioning as (a) monodentate and as (b) bridging ligand but not as chelating ligand, its silver(II) complexes are of added interest. The pyrazine (pyz) complex of empirical composition $[Ag(pyz)_2]S_2O_8$ is, by analogy to the four coordinate planar tetra(pyridine)silver(II) persulphate is formulated as a square planar



(29-VIII)



(29-IX)



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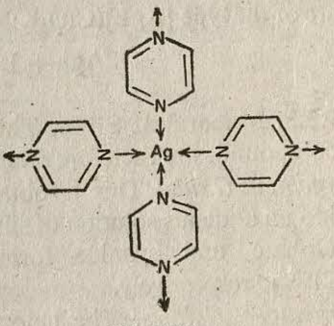

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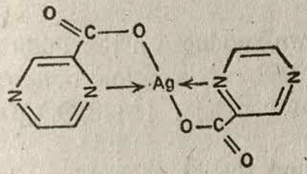

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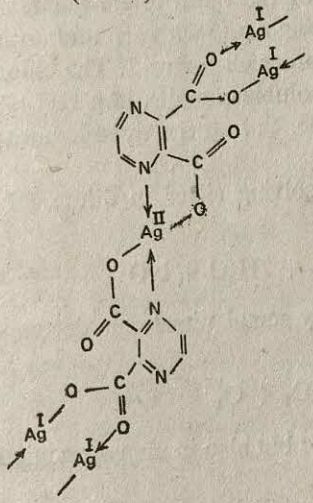
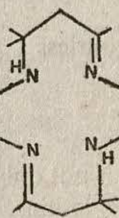


(29-XIII)



(29-XIV)

polymer (20-XII). Note that each silver (II) claims only half share of the four pyz molecules. Bis(pyrazine-2-carboxylato)silver(II) (29-XI) is magnetically dilute, monomeric and isostructural with bis(picolinato)silver(II). Pyrazine 2, 3 dicaroxylic acid forms an unusual silver complex (29-XIII) which contains both silver (I) and silver (II) in the ratio 2:1. All these compounds are obtained by peroxydisulphate oxidation of silver nitrate in presence of the ligands. Their colours are dark red to red brown and they are paramagnetic. The identities of the complexes have been established through oxidimetric titration, magnetic moment, infrared spectra and *d-d* transition ($4d^9$ system; cf copper (II)).

A novel method of synthesis of silver (II) complex via disproportionation of silver (I) into silver (II) and metallic silver in the presence of macrocylic tetraaza ligands (L; 29-XIV) has been described. The complexes are orange, paramagnetic and are of the type $[AgL](ClO_4)_2$;

$$2Ag^+ + L —— [AgL]^{2+} + Ag^0$$

29.3.3. Monovalent Silver. This oxidation state is a $4d^{10}$ system and all argentous compounds are therefore diamagnetic.

Argentous Oxide: This is obtained as a brown product on the addition of alkali to an aqueous solution of silver nitrate. It dissolves in solutions of ammonia, thiosulphate and cyanide forming soluble $Ag(NH_3)_2]^+$, $[Ag(S_2O_3)_2]^{2-}$ and $[Ag(CN)_2]^-$ respectively.

Argentous Halides: The chloride, bromide and the iodide are precipitated from aqueous silver salts on the addition of the appropriate halide ion. The fluoride is soluble and is obtained by neutralising Ag_2O with HF and crystallising. The solubility in aqueous medium falls in the order Cl $>$Br$>$I. The chloride and the bromide dissolve in ammonia to give the soluble complex $[Ag(NH_3)_2]X$ (X = Cl, Br) but the iodide is only sparingly soluble. But all the three halides dissolve in excess KCN.

Argentous Nitrate: It is prepared by dissolving silver in dilute HNO_3 and evaporating to crystallisation:

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + 2H_2O + NO$$

This forms colourless crystals. Like all heavy metal nitrates it decomposes on heating:

$$2AgNO_3 \rightarrow 2Ag + 2NO_2 + O_2$$

The compound is not only very soluble in water but also in many organic solvents such as pyridine, aniline, acetonitrile etc.

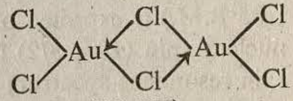
Argentous Complexes: Like copper (I), silver (I) is also a soft acid and therefore, prefers to bind better with soft donors. Its most usual coordination number is 2 (linear) with *sp* hybridisation. In a few cases coordination number 3 (sp^2) and coordination number 4 (tetrahedral sp^3) are known. The linear coordination is achieved with an L—Ag—L angle 180°; so that a bidentate chelating ligand cannot help to achieve this coordination. Thus AgCl reacts with ethylenediamine to give a dimeric species with ethylenediamine functioning as a bridging ligand instead of chelating one eg: $Cl-Ag \leftarrow NH_2-(CH_2)_2-NH_2 \rightarrow Ag-Cl$. Tetrahedral complexes $[AgL_4]ClO_4$ (L = R_3P; phosphites) and thiourea (L) complexes, $[AgL_2]X$, are also known.

29.4. OXIDATION STATES OF GOLD

24.4.1. Trivalent Gold. The + 3 oxidation state in gold is stabler than the +1 state. The +3 state has a very strong tendency to complexation. Indeed simple or aquo Au^{3+} does not occur. It exists in complexes with coordination number 4. In rare cases higher coordination numbers are observed.

Auric Hydroxide: Treatment of $AuCl_4^-$ solution by a base gives a yellow-brown precipitate $Au(OH)_3$. This is weakly acidic as is shown by its dissolution in alkalies to give $Au(OH)_4^-$ or AuO_2^-. The hydroxide is often called auric acid.

Auric Chloride: Reaction between chlorine and gold metal at ~200°C gives dark red crystals of auric chloride. Auric chloride is a dimer (29-XV) as shown by molecular weight measurements. When gold is dissolved in aqua regia and the solution concentrated chloroauric acid $H[AuCl_4].4H_2O$ crystallises. Salts such as $K[AuCl_4]$ are also known.



(29-XV)

Auric Bromide: This is a dark brown compound obtained by the interaction of gold and bromine. Molecular weight determination of the compound (by elevation of boiling point of bromine) gives a dimeric formula Au_2Br_6. The compound reacts with bromide ions to give tetrabromoaurate ion.

Auric Iodide: The compound seems to have been obtained by the careful addition of aqueous auric chloride to KI when $K[AuI_4]$ is obtained, which is then treated with $AuCl_3$:

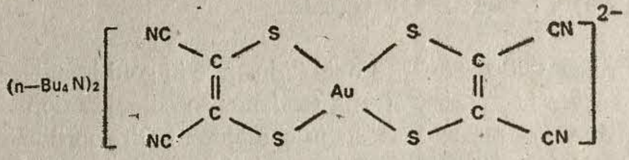
$$3K[AuI_4] + AuCl_3 \rightarrow 4AuI_3 + 3KCl$$

The compound is dark green, insoluble in water and slowly decomposes to give aurous iodide.

Complexes: Substitution reactions on $AuCl_4^-$ lead to the syntheses of many types of complexes: $[AuCl_2py_2]Cl$, $[Au(o\text{-}phen)Cl_2]Cl$, $[Au(dien)Cl]Cl_2$, $[Au(diars)_2]Cl_3$ etc. A few compounds with higher coordination numbers have been reported: $[Au(diars)_2I_2]I$, $[Au(diars)_2I]I_2$. The compounds are all coloured yellow to orange. The four coordinated auric compounds are square planar with dsp^2 hybridisation, and are diamagnetic.

29.4.2. Bivalent Gold: Copper (II) is $3d^9$ while gold (II) is $5d^9$. In view of the fact that 10 *Dq* rapidly increases from the first transition series to the second and then to the third, it follows that for the same ligand set in a tetragonal stereochemistry the ninth electron of gold (II) will be at a much higher energy (cf: Part I: page 236; first para and Fig 10.15) than copper (II). Hence the ninth electron will be prone to oxidation. This explains the ready disroportionation of gold (II) to gold (III) and gold (I).

Despite the tendency of gold (II) to disproportionate into gold (I) and gold (III) a limited few gold (II) complexes have very recently been claimed. One such complex is the tetra *n*-butylammonium salt of the bis(maleonitriledithiolato)gold(II) anion shown below:



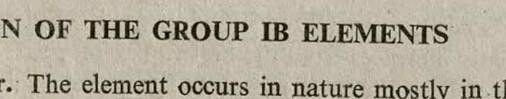
(29-XVI)

The above complex, $(n\text{-}Bu_4N)_2$ $[Au(mnt)_2]$ has been prepared by the borohydride reduction of the corresponding gold (III) complex. Its magnetic moment ($\mu_{eff} \simeq$ 1.85 B.M.) is expected of a $5d^9$ system. The unpaired electron interacts with the nuclear spin ($I = 3/2$) of 197-gold and gives, as expected, a four line electron spin resonance spectrum (cf. Appendix V). Some authors claim that the unpaired electron resides on the ligand (radical) rather than on gold. *o*-Aminobenzenethiol (abt H) reasts with $HAuCl_4$ to give a violet, paramagnetic dimer $[Au(abt)_2]_2$. This complex gives a seven line ESR spectrum.

29.4.3. Monovalent Gold. Although the charge is small no simple cation exists. Most compounds are insoluble in aqueous medium. Most of these have covalent links or are in the form of complexes. These are usually obtained from gold (III) by reduction with excess ligand or by the agency of a reducing agent.

AuCl is obtained by heating $AuCl_3$ to 200°C. Aurous bromide is also obtained by the thermal decomposition of $AuBr_3$ at 115°C. Aurous iodide can be obtained by the reduction of AuI_3 by HI or by the action of excess KI on $AuCl_4^-$. Like copper (I) and silver (I) halides the solubilities of gold (I) halides are low and the solubility decreases from the chloride to the iodide.

This oxidation state is stabilised enormously in the cyano complex $Au(CN)_2^-$. The complex has high formation constant ($K \sim 10^{28}$). The formation of this complex is utilised in the extraction of the element. Trivalent phosphorus ligands first reduce gold (III) to gold (I) and then forms complexes eg: $R_3P \rightarrow Au{-}Cl$. Gold (I) being a soft acid prefers to complex with soft donors such as sulphur, phosphorus etc:



$$\begin{array}{l} CH_2{-}NH \\ | \\ CH_2{-}NH \end{array}\!\!\!\Big\rangle S \rightarrow AuX : (C_2H_5)_2S \rightarrow Au{-}X$$

29.5. ISOLATION OF THE GROUP IB ELEMENTS

29.5.1. Copper. The element occurs in nature mostly in the form of cuprous sulphide or cuprous/cupric oxides: *chalcocite* (Cu_2S), *copper pyrites* ($Cu_2S.Fe_2S_3$), *cuprite* (Cu_2O), *malaconite* (CuO), *malachite* ($CuCO_3.Cu(OH)_2$) etc.

The element is recovered from sulphide ores by the following procedure. The ore is first crushed and concentrated by froth floatation process. The ore is then roasted in a current of air to remove arsenic and antimony contaminants as volatile oxides. During the process some sulphur is also oxidised:

$$Cu_2S.Fe_2S_3 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$$

The roasted ore is then introduced into a blast furnace together with a little coke and silica (sand) and is fused. This step converts FeS to FeO which then combines with silica to form a slag:

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2 \ ; \ FeO + SiO_2 \rightarrow FeSiO_3$$

The slag floats above the layer of cuprous sulphide (mixed with some FeS), which is called the *matte*. The matte is then introduced into a Bessemer converter. A blast of air and sand is blown through the hot matte. The iron sulphide, that had escaped oxidation so far, now gets oxidised to FeO which again forms a slag. The cuprous sulphide gets partially converted to Cu_2O which then reacts with Cu_2S to give Cu:

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2 \ ; \ Cu_2S + 2Cu_2O \rightarrow 6Cu + SO_2$$

The copper is obtained in a fused state and is run off into moulds of sand to form *blister copper*, which is about 98% pure copper. As the molten copper cools and solidifies the trapped SO_2 escapes and while doing so leaves *blisters* or *scars* on copper.

The impure blister copper is purified by electrolytic method. The impure copper is cast into plates which are suspended into lead-lined tanks containing cupric sulphate and dilute H_2SO_4. The impure plates are made the anode, and thin plates of pure copper serve as cathodes. The cathode plates are coated with graphite so that fresh deposit of pure copper on them can be easily removed. On electrolysis, the more electropositive (basic) elements such as zinc, iron, nickel etc. stay in solution as ions. Less basic ones, that is more noble metals such as gold and silver, are left undissolved and settle to the bottom of the electrolytic cell, and are removed as *anode mud*. Pure copper deposits on the graphite-coated cathodes.

at the *anode* : $Cu \rightarrow Cu^{2+} + 2e$

at the *cathode* : $Cu^{2+} + 2e \rightarrow Cu$

If the above electrode reactions were the only reactions one would expect there would be deposited as much copper on the cathode as would dissolve from the anode. Furthermore there would occur no change in the concentration of H_2SO_4. Actually the concentration of copper (II) in solution increases and that of H_2SO_4 decreases. This is due to the fact that part of the copper dissolves from the anode in the cuprous state. Dissolution of copper as copper (I) would require half the electrical energy compared to $Cu \rightarrow Cu^{2+} + 2e$ process. If all the copper (I) had migrated to the cathode we would have found no change in copper concentration of the electrolyte. Copper (I) is oxidised to copper (II) by (a) dissolved oxygen in the presence of H_2SO_4, and (b) by disproportionation:

$$\text{(a) } Cu_2SO_4 + H_2SO_4 + \tfrac{1}{2}O_2 \rightarrow 2CuSO_4 + H_2O$$
$$\text{(b) } Cu_2SO_4 \rightarrow CuSO_4 + Cu$$

Some copper therefore appears as anode mud at the bottom of the cell.

29.5.2. Silver. The important ores of silver include *argentite* (Ag_2S), *horn silver* ($AgCl$), *pyrargyrite* (thioantimonite, Ag_3SbS_3) etc.

Silver is mostly worked out from sulphide ores, and the commonest procedure is the cyanide extraction. The finely ground ore is agitated with air and a dilute (1%) NaCN solution for many hours. The silver gradually goes into solution as sodium argentocyanide:

$$Ag_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S$$

The air serves to oxidise the sodium sulphide to sulphate and thus forces the reaction to go over to the right. If the ore contains any AgCl, that too undergoes a similar reaction:

$$AgCl + 2NaCN \rightarrow Na[Ag(CN)_2] + NaCl$$

The silver is now precipitated from the argentocyanide solution by the addition of zinc dust:

$$2Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Ag$$

The silver is finally collected and fused with KNO_3 to oxidise any zinc that may be present as a contaminant. Purification of silver is also done by an electrolytic procedure comparable to that of copper. The anode consists of plates of impure silver, the cathode is composed of pure silver and the electrolyte contains silver nitrate and nitric acid.

29.5.3. Gold. The element occurs mostly in the native state, and to a lesser extent as sulphide, arsenide and as telluride. The modern method for its extraction is analogous to the cyanide process for silver. Very dilute solution of NaCN, and air are used to agitate the finely divided gold-bearing material when sodium aurocyanide is formed:

$$4Au + 2H_2O + O_2 + 8NaCN \rightarrow 4Na[Au(CN)_2] + 4NaOH$$

The solution is then run through boxes of zinc turnings when gold is precipitated as a black material:

$$2Na[Au(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Au$$

Treatment with sulphuric acid removes zinc and any silver that may be present in the starting material. Finally pure gold is obtained by electrolysis of an aurocyanide solution.

The metal has the highest positive standard potential in the subgroup. Thus it is not acted upon by common acids but dissolves in aqua regia due to oxidation:

$$HNO_3 + 3HCl \rightarrow 2H_2O + ClNO + Cl_2; 2Au + 2HCl + 3Cl_2 \rightarrow 2H[AuCl_4].$$

29.6. USES OF THE GROUP IB ELEMENTS

Copper: This finds extensive use as an engineering material. Its importance results from its high thermal and electrical conductivities and from its malleability, ductility and resistance to corrosion. Boilers, stills, condensers, kitchen utensils are often made of copper. It is also used in the manufacture of electrical machinery, wire, transmission lines etc. Alloys of copper also find important uses. *Brasses* (Cu, 60–80%; Zn, 40–20% together with other constituents in smaller percentage) are used in utensils, cartridge cases, castings etc. *Bronzes* are composed mostly of copper (75–90%) and tin (25–10%) together with other minor constituents. These are used in coins, statues, machineries etc. Bronzes are stronger and are more resistant than pure copper. *German silver* (Cu, 25–50%; Zn, 35–25%; Ni, 35–10%) is used in plates, oranaments etc. *Monel metal* (Cu, 30%; Ni, 67%; Fe + Mn, 3%) is used in acid pumps, acid containers etc.

Silver: This is widely used in coins usually in the form of an alloy with copper (7–10%). Copper serves to increase the hardness of the alloy and helps to improve its wearing qualities. It is also extensively used in jewellry, silver plated cutlery and other table ware. Silver salts are also valuable in silver mirroring.

Silver Plating: The article to be silver plated is made the cathode of an electrolytic cell, a piece of pure silver is made the anode and the electrolyte is a solution of sodium argentocyanide $Na[Ag(CN)_2]$. The complex cyanide dissociates to a small extent to produce a low concentration of silver ion in the electrolyte. The low concentration of silver ion favours the formation of a smooth coherent deposit. More soluble silver salts such as $AgNO_3$ will produce a loose, crystalline, non-adherent deposit.

Silver Mirroring: This is done by depositing a coating of metallic silver on one surface of a piece of glass. This is usually achieved by reduction of a solution containing $[Ag(NH_3)_2]^+$ with formaldehyde.

Photography: Photographic films or plates contain an emulsion of silver bromide (with little silver iodide), which is prepared by mixing solutions of silver nitrate and ammonium bromide with gelatine. On exposure the silver salt becomes more readily reducible to the metallic state, the reducibility being proportional to the intensity of light that falls on different areas of the plate or film. The exposed film or plate is then immersed in a '*developer*' bath which contains a solution of a very mild reducing agent. The reducing agent (potassium ferrous oxalate, pyrogallol) is without effect on the unexposed parts of the film, and further the reducing effect is also the fastest where the exposure intensity is the highest. The plate thus becomes darkest where the intensity is the highest. The next operation is to treat the 'negative' as obtained in the last step, with a solution of sodium thiosulphate ('hypo') to dissolve out the silver bromide which has not been light-activated and reduced. This step is known as *fixing*, and the dissolution occurs due to the formation of a soluble thiosulphato complex:

$$AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$$

The negative, thus fixed, is then printed. The printing-out-paper is an emulsion of silver chloride in egg albumin. It is exposed through the negative, so that the bright and dark spaces are reversed, and the shading of the photograph becomes the same as that of the original object. Fixing and developing are again carried out.

Gold: Because of a bright colour and chemical inactivity gold has been preferred in ornaments and coins. However it is used in alloys commonly with copper to increase its hardness. The gold content of alloys is expressed as '*Carat*', which *indicates the number of parts by weight of gold in 24 parts of the alloy*. Thus 1-0 Carat gold means 10/24 fraction of gold, that is, ~ 41 % gold.

29.7. ANALYTICAL REACTIONS OF THE GROUP IB ELEMENTS

Copper: This appears in group IIA of the qualitative scheme. It is precipitated as the sulphide CuS in presence of dilute HCl, and is finally detected by the deep blue colour of $[Cu(NH_3)_4]^{2+}$ obtained in presence of ammonia.

For quantitative estimation it may be reduced by SO_2 in dilute acid medium and cuprous copper precipitated as CuSCN by the addition of thiocyanate. The precipitate can then be weighed. For volumetric determination a cupric salt is treated with potassium iodide in dilute acetic acid medium and the liberated iodine titrated against thiosulphate.

Silver: The element gives an insoluble chloride with HCl. Hence it is included in group I of the qualitative scheme. The white AgCl precipitate dissolves in ammonia and reappears on making the solution acidic with HNO_3.

Gravimetric estimation of silver also involves its precipitation as AgCl in presence of dilute HNO_3. The precipitate is allowed to stand in subdued light overnight, then filtered, washed with very dilute HNO_3, dried and weighed.

Gold: An important test for gold is to treat a dilute solution of the gold compound with a solution of a mixture of $SnCl_2$ and $SnCl_4$. On heating reduction to elementary gold occurs in the form of a deep purple precipitate known as *purple of Cassius*. The precipitate is colloidal gold adsorbed on colloidal stannic acid.

For gravimetric estimation the gold solution is reduced by SO_2 in dilute HCl medium. After digestion on a steam bath the precipitated gold is collected and weighed. The gold solution should be free from lead, selenium and tellurium.

STUDY QUESTIONS

1. From a comparative assessment of the alkalies and the currency metals show that Mendeleev's classification of allowing Group IA and Group IB the same column in the Periodic Table is not a happy one.

2. From a study of the elements show that copper, silver and gold can be considered as transition elements although they have a filled *d*-subshell in their atomic state.

3. Copper (II) is common oxidation state of copper but silver (II) is an uncommon oxidation state of silver. In an answer to this difference let us assume that by virtue of bigger sized *d*-orbitals spin pairing is facilitated in silver and hence it is more difficult to extract electron from the filled *d*-subshell. Do you agree? Is this explanation helpful for other transition groups?

4. Taking silver (II). silver (III) and copper (III) as typical less familiar oxidation states, present a coherent picture of the requirements of stabilisation of such states.

5. On the addition of ammonia to a cupric solution an intense blue colour is formed whereas on heating $CuSO_4.5H_2O$ to ~ 150°C the blue colour is almost gone ! How do you explain?

6. What is a δ-bond? How does it differ from a σ-bond and a π-bond?

7. Discuss the structures of copper (II) sulphate pentahydrate and copper (II) acetate monohydrate.

8. $K_3[CuF_6]$ is paramagnetic while $K[AgF_4]$ is diamagnetic. Explain.

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30

Group IIB. Zinc, Cadmium and Mercury

Zinc, cadmium and mercury belong to Group IIB of the Periodic Table. All the three elements occur in nature as sulphides. Their relative abundances are: zinc, (0.02%), cadmium (2×10^{-5}%) and mercury ($\sim 10^{-4}$%).

30.1. COMPARATIVE STUDY OF THE GROUP IIB ELEMENTS

30.1.1. General Considerations. Zinc, cadmium and mercury appear after copper, silver and gold in their respective periods. Their electronic configurations have a $d^{10}s^2$ distribution in the two outermost subshells. Experimental studies have shown that the predominant valence is + 2 with the d^{10} subshell remaining intact. No oxidation state is known where there exists any incomplete d level. Hence these elements are excluded from the list of regular transition elements. In fact none of these elements shows the characteristic features of the transition elements namely variable valence, coloured compounds and paramagnetic complexes. The apparent case of a second valence with mercury, that of mercurous mercury, is due to an inert pair effect.

The sum of the first two ionisation potentials is slightly higher than those of copper, silver and gold. Although the gap between the first and the second potential for the three elements is wide enough no definite evidence is available for the existence of univalent zinc and cadmium. Contrary to what we usually find for regular, non-transition elements the sum of the two potentials does not fall from zinc to mercury, instead it increases (Table 30.1). This points to the increasing noble character of the elements, which trend is also shown by the change of the standard potential from negative to positive values. Expectedly zinc and cadmium liberate hydrogen from acids but not mercury. The standard potentials would allow us to predict that zinc should be the most basic but this is not entirely true.

Note that both cadmium and mercury have almost the same atomic size although they have widely varying atomic numbers. The result of this is an almost two-fold increase in the density of mercury compared to that of cadmium (Table 30.2).

The high ionisation potential of mercury would militate against this element showing many ionic compounds. In fact mercury (II) has a flair for forming strongly covalent compounds. Therefore complex formation is more abundant with mercury than cadmium or zinc.

Table 30.1. Electronic Configuration and Some Properties of Group IIB Elements

Element	Atomic Number	Electronic Configuration	Ionisation Potential (*ev*)	Electro-negativity
Zinc	30	$[Ar]3d^{10}4s^2$	9.39, 17.96, 39.70	1.6
Cadmium	48	$[Kr]4d^{10}5s^2$	8.99, 16.90, 37.47	1.7
Mercury	80	$[Xe4]f^{14}5d^{10}6s^2$	10.43, 18.75, 34.2	1.8

Table 30.2. Some More Properties of Group IIB Elements

Element	Atomic Radius(A)	Ionic(M^{2+}) Radius(A)	M.P. (°C)	B.P. (°C)	Density (g,/ml)	E° (volts) $M^{2+} + 2e \rightleftharpoons M$
Zinc	1.33	0.69	419	907	7.1	-0.763
Cadmium	1.49	0.92	321	767	8.61	-0.403
Mercury	1.50	0.93	-38.9	357	13.55	$+0.789$

Group IIA of the Periodic Table contains the regular non-transition elements Be, Mg and the alkaline earths. All these IIA elements possess an outermost s^2 configuration but underneath this subshell there are no filled *d*-orbitals but only *s* and *p*-orbitals. The alkaline earths are next to the alkalies in their electropositive character but beryllium and magnesium are much less electropositive. All these elements show also one valence, namely + 2. By virtue of a very small size Be is extremely complex forming—which tendency falls down the group. All these elements have negative standard potentials and the values become more negative with increasing atomic number. It is to be noted that the ionisation potentials of the elements fall down the group (Chapter 15).

30.1.2. Chemical Behaviour. *Hydrides:* The hydrides of these elements are of the interstitial type. Although the elements are not transition elements they are not strongly basic either to give ionic hydrides.

Oxides and Hydroxides: Zinc hydroxide is really amphoteric. Zinc not only dissolves in acids but also dissolves in alkali to form zincate ions ZnO_2^{2-}. $Cd(OH)_2$ is more basic than $Zn(OH)_2$ whereas $Hg(OH)_2$ is an extremely weak base. It should be mentioned that no $Hg(OH)_2$ has really been isolated but it is generally believed to be the species resulting from the dissolution of the sparingly soluble mercuric oxide in water.

Halides: The fluorides of the elements are ionic in nature. All other halides, particularly those of mercury (II), are covalent. All the three elements form halo complexes, those of mercury (II) being the stablest. $HgCl_2$ remains in aqueous solution as covalently bonded $HgCl_2$, which is shown by its non-electrolytic conductance. The conductivity of cadmium halide solution distinctly falls with increasing concentration. This is attributed to the change from aquo cadmium (II) ions and halide ions in dilute solution to species like $[CdX]X$, $Cd[CdX_4]$ etc. thus causing the conductivity to fall. A moderately concentrated solution of CdI_2 shows conductance of a bi-bivalent electrolyte, which means that $Cd[CdI_4]$ is the predominating species in solution.

Complexes: Although in their bipositive state the elements have filled *d*-orbitals these cannot lead to the formation of π-acid complexes. The + 2 charge does not favour transfer of electron density from the metal ion to the π-acid ligands. Thus no carbonyls, nitrosyls, etc are known. However there is no diffculty in their forming usual complexes with L → M sigma donation.

Commonest complexes are either linear (*sp* hybridisation) or tetrahedral (sp^3 hybridisation). Higher coordination numbers are little known. Considerable covalent character appears in mercury-ligand links. Also recall that these ions are rather soft acids so that they form stronger complexes with soft bases, that is, with phosphorus, sulphur and heavier halogen donors. That the mercury (II) complexes are much more stable than those of cadmium (II) and zinc (II) are shown by an inspection of the stability constants of the tetrahalo complexes:

$$M^{2+} + 4X^- \rightleftharpoons [MX_4]^{2-};\ K = \frac{[MX^{2-}_4]}{[M^{2+}]\,[X^-]^4}$$

X	Zn^{2+}	Cd^{2+}	Hg^{2+}
Cl	1	10^3	10^{16}
I	10^{-2}	10^6	10^{30}
CN	10^{16}	10^{18}	10^{41}

30.2. PECULIARITIES OF MERCURY

In this subgroup zinc and cadmium are rather close to each other but they differ widely from mercury. For example, whereas low conductivity of cadmium halides in water is due to *autocomplex formation* ($2CdCl_2 \rightleftharpoons Cd[CdCl_4]$), there is no evidence for the existence of $Hg[HgCl_4]$. Instead, no electrolytic nature of mercuric chloride arises from undissociated covalently linked Cl—Hg—Cl molecules. Above all mercury has a peculiar valence state in its mercurous compounds with a metal—metal covalent link $(Hg-Hg)^{2+}$ which has no parallel in the entire metal chemistry. The peculiarities of mercury are enumerated below:

1. *High Ionisation Potential:* The first ionisation potential (10.43 *ev*) is the highest first I.P. of all metals. The only other elements which have higher ionisation potentials are hydrogen (13.53 *ev*), carbon, noble gases and the electronegative elements of nitrogen, oxygen and fluorine families. Thus mercury is to be considered as a noble metal. This is also supported by its positive standard electrode potential (+0.789 volts).

2. *Volatility:* Mercury is the most volatile metal in the Periodic Table. The melting points and boiling points of the three most volatile metals are given below:

	Cs	Ga	Hg
M.P. (°C)	28.5	29.8	−38.9
B.P. (°C)	705	2030	357

Mercury vapour is monatomic.

3. *Amalgam Formation:* Mercury has a strong power of forming liquid metallic solution or *amalgam*. This property of forming metallic solution is also to be found with other metals above their melting points. In the case of mercury this is of special importance because of its very low melting point. Some of the amalgams have distinct melting points and conform to definite composition such as Hg_2Na, Hg_2K etc. Alkali metal amalgams are among the most useful reducing agents.

4. *Valence State in Mercurous Compounds:* Besides the usual group valence +2, mercury exhibits a peculiar unparalleled valence state in the mercurous compounds. This state is correctly represented as Hg_2^{2+} and *not* as Hg^+. The following experimental evidences support this formulation.

(*a*) Variation of conductance with dilution of mercurous nitrate $Hg_2(NO_3)_2$ resembles that of a bi-univalent electrolyte $Pb(NO_3)_2$ rather than a uni-univalent electrolyte $AgNO_3$.

(*b*) X-ray crystal structure determinations of several mercurous compounds show that there is a strong Hg—Hg bond, the bond length being ~2.5A (atomic radius of Hg = 1.50A).

(*c*) Monatomic formulation like HgCl is ruled out by the diamagnetic behaviour of all mercurous salts. Mercury (I) with 79 electrons must possess one spin giving paramagnetic (1.73 B.M.) behaviour. Instead Hg_2^{2+} $((Hg-Hg)^{2+})$ will be diamagnetic due to spin pairing arising out of the covalent link between the two mercury atoms.

(*d*) Various studies of the equilibrium constants of the following two reactions (1) and (2) also point to the correct formulation Hg_2^{2+}. Mercuric nitrate

$$2Hg^+ \rightleftharpoons Hg + Hg^{2+} \quad \ldots (1)$$

$$\frac{[Hg^{2+}]\,[Hg]}{[Hg^+]^2} = \text{constant}$$

$$\frac{[Hg^{2+}]}{[Hg^+]^2} = \frac{\text{constant}}{[Hg]} = K_1$$

$$Hg_2^{2+} \rightleftharpoons Hg + Hg^{2+} \quad \ldots (2)$$

$$\frac{[Hg^{2+}]\,[Hg]}{[Hg_2^{2+}]} = \text{constant}$$

$$\frac{[Hg^{2+}]}{[Hg_2^{2+}]} = \frac{\text{constant}}{1} = K_2$$

solution is treated with metallic mercury when an equilibrium is reached between Hg, Hg^{2+}, Hg_2^{2+} (or Hg^+). The concentration of mercury ([Hg]) does not vary, and becomes part of the equilibrium constant. The values of K_1 and K_2 are calculated from solutions of different initial concentrations of mercuric salt. K_2 alone remains substantially constant and not K_1. The value of K_2 is $\sim 1/116$, that is, the equilibrium ratio of Hg_2^{2+} to Hg^{2+} in presence of mercury is 116. Such equilibrium value indicates that wherever a mercuric salt is far less soluble than the corresponding mercurous salt, the latter has to disproportionate into metallic mercury and the mercuric salt in order to maintain the ratio close to 116. Thus any reagent that leads to a decrease in the concentration of Hg^{2+} in solution will enhance the conversion of Hg_2^{2+} into Hg and Hg^{2+}.

30.3. MERCUROUS STATE AND INERT PAIR EFFECT

A good degree of stability or inertness is associated with the s^2 pair of electrons in the noble gas helium. Certain non-transition elements often show chemical behaviours which are explicable only on the assumption of a model that their s^2 pair of electrons is inert. Their chemistries show as if the s^2 pair have become a part of the inner core of electrons. We have already noted such examples in indium, thallium, tin and lead. These elements have an s^2p or s^2p^2 configuration and their valences change by two units depending on whether or not the s^2 pair of electrons participate in chemical reactions:

Indium	[Kr]	$4d^{10}5s^25p^1$	valences :	1 and 3
Thallium	[Xe]	$4f^{14}5d^{10}6s^26p^1$	valences :	1 and 3
Tin	[Kr]	$4d^{10}5s^25p^2$	valences :	2 and 4
Lead	[Xe]	$4f^{14}5d^{10}6s^26p^2$	valences :	2 and 4

The inert pair effect is also shown in mercury but in a very unique way. Note that mercury has only two valence electrons ($6s^2$). If both these are to become inert valence becomes redundant. Two s electrons of two mercury atoms become unavailable for valence purposes through a strong Hg—Hg link, thus leaving two other electrons available for bonding purposes. In the covalent Hg_2Cl_2 the two mercury atoms form two linear *sp* hybrid orbitals. Each of these hybrid orbitals carries one spin. Overlap of two such orbitals makes the mercury—mercury link. The two remaining orbitals with one spin on each overlap with chlorine orbitals with one spin on each.

30.4. ZINC AND CADMIUM COMPOUNDS

30.4.1. Zinc Oxide. Zinc burns in air on heating to give zinc oxide. Presence of lead as impurity imparts a yellow colour due to litharge. To obviate the yellow colour the impure zinc metal is heated in a mixture of CO_2 and air whereby white lead carbonate is formed alongwith zinc oxide. Zinc oxide is also prepared from carbonate ore by heating with carbon in a blast of air. The carbon reduces the ore to metallic zinc which volatilises leaving the non-volatile impurities (iron, manganese etc). The zinc vapour is oxidised immediately to ZnO which is carried along as a fine dust in the flue gases. It is then collected in filter bags.

$$ZnCO_3 \rightarrow ZnO + CO_2 \; ; \; ZnO + C \rightarrow Zn + CO$$
$$2Zn + O_2 \rightarrow 2ZnO$$

Zinc oxide is extensively used as a white pigment under the trade name *chinese white*. This pigment is superior to white lead since with H_2S it does not turn black. It is also used in zinc ointment and in making glazes for some porcelain wares.

30.4.2. Zinc Hydroxide. This is precipitated on the addition of alkali to a zinc salt. It is amphoteric and dissolves in acids to give zinc salts, and in alkalies to form zincate ions. The zincate ion is commonly written as ZnO_2^{2-} but a more reasonable formulation in solution would be $[Zn(OH)_3(H_2O)]^-/[Zn(OH)_4]^{2-}$ allowing a coordination number four. In fact solid zincate with the formula $Na_2[Zn(OH)_4]$ has been obtained from concentrated solutions. Metallic zinc also dissolves in alkalies with liberation of H_2 and formation of zincate ions:

$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2; Zn(OH)_2 + 2NaOH \rightarrow Na_2[Zn(OH)_4]$$

Zinc hydroxide dissolves in ammonia to form a tetrammine complex $[Zn(NH_3)_4]^{2+}$.

30.4.3. Zinc Chloride. On a commercial scale zinc chloride is made by dissolving metallic zinc in excess HCl. The solution is evaporated till the temperature rises to 230°C, when the liquid consists of fused $ZnCl_2$. The liquid is then crystallised in airtight containers. Presence of excess HCl prevents hydrolysis ($ZnCl_2 + H_2O \rightarrow Zn(OH)Cl + HCl$). The compound is extremely hygroscopic. It can prevent rotting of timber and therefore it is used to impregnate railroad sleepers. Because of its ability to dissolve metallic oxide this is used as a flux in soldering

Depending on concentration, an aqueous solution of $ZnCl_2$ may contain several species: $[Zn(H_2O)_6]^{2+}$, $[ZnCl(H_2O)_5]^+$, $[ZnCl_2(H_2O)_4]$ and even $[ZnCl_4(H_2O)_2]^{2-}$ but not $[ZnCl_4]^{2-}$.

30.4.4. Zinc Sulphate. This is the commonly known white vitrol, $ZnSO_4 . 7H_2O$. This is readily obtained by dissolving the metal in dilute H_2SO_4 and crystallising. The most important use of the salt is in the manufacture of a white pigment called *lithopone*. This pigment, a mixture of ZnS and $BaSO_4$, is made by the reaction of $ZnSO_4$ and BaS:

$$ZnSO_4 + BaS \rightarrow ZnS + BaSO_4$$

The precipitated mass is dried and powdered. Lithopone is much used in wall painting. It has a good covering power, is not very expensive and is not blackened by H_2S. This is also used in preservation of hides.

30.4.5. Zinc Sulphide. This is obtained as a precipitate on the passage of H_2S through an ammoniacal solution of a zinc salt:

$$ZnSO_4 + H_2S + 2NH_4OH \rightarrow ZnS + (NH_4)_2SO_4 + 2H_2O$$

No precipitate of ZnS appears in an acid medium since the solubility product of ZnS cannot be exceeded. It finds use as a constituent of lithopone. In presence of trace impurities of copper or managanese sulphides this becomes luminiscent. After exposure to light, the sulphide (prepared by passing H_2S through an ammoniacal solution of a zinc salt containing a small amount of a manganese salt) becomes luminous in the dark. On exposure to alpha rays also it becomes luminous. The luminous dials of watches are painted with zinc sulphide containing about 1 part in 10 million of a radium salt serving as an alpha ray source.

30.4.6. Cadmium Oxide and Hydroxide. The oxide is obtained by heating the metal in air or by heating the hydroxide, carbonate or nitrate. Depending on the mode of heating its colour varies from greenish yellow to brown.

Cadmium hydroxide is precipitated as a white product on the addition of a hydroxide to the solution of a soluble salt. It is more basic than $Zn(OH)_2$ and does not dissolve in excess alkali. How ever like zinc hydroxide it dissolves in ammonia forming cadmium tetrammine complex.

30.4.7. Cadmium Chloride. It can be obtained by dissolving the base in HCl and crystallising. Cadmiumchloride (and also the other cadmium halides) behaves as weakly dissociated electrolyte in aqueous solution. There are significant amounts of undissociated chloride $CdCl_2$ present in concentrated solution but autocomplex formation is also a dominating feature:

$$2CdCl_2 \rightleftharpoons Cd^{2+}[CdCl_4]^{2-}$$

30.4.8. Cadmium Sulphate. It is obtained by dissolving the hydroxide in dilute H_2SO_4 and crystallising as $CdSO_4.8/3\ H_2O$. The normal heptahydrated vitriol can be obtained but it always loses water to revert to the 8/3 H_2O species. Cadmium sulphate is used in the manufacture of standard Weston cadmium cells and in alkali batteries.

30.4.9. Complexes of Zinc and Cadmium. The $+2$ states of these elements possess a filled *d*-subshell. An appreciation of the splitting of the five *d*-orbitals (with 10 electrons) in an octahedral ($t^6_{2g}\, e^4_g$) or in a tetrahedral ($e^4 t^6_2$) geometry shows that the ions gain no special crystal field stabilisation energy (CFSE) in either octahedral field (CFSE $= 6\times(-4\,Dq) + 4\times(+6\,Dq) = 0$) or in a tetrahedral field (CFSE $= 4\times(-6Dq_t) + 6\times(+4\,Dq_t) = 0$). As against these cases we may check the case of Co^{3+} ion in a low spin state in an octahedral geometry ($t_{2g}{}^6 e_g{}^0$; CFSE $= 6\times(-4\,Dq) = -24\,Dq$). This explains why cobalt (III) forms so readily spin paired octahedral complexes. Since filled d^{10} ions have no such CFSE they possess no preference for any stereochemistry on crystal field grounds. *Their stereochemistries and coordination numbers are therefore dictates of ligand—ligand repulsion and size of the ions. Thus we find these elements mostly assume a four-coordinate tetrahedral geometry since in this geometry ligand-metal-ligand bond angles are larger than in square planar or octahedral geometry*. However a coordination number 2 with *sp* hybridisation is known in a few cases. Five coordinate (square pyramidal or trigonal bipyramidal) complexes are known with zinc(II). Zn^{2+} tends to form stronger bonds to F and O whereas Cd^{2+}, being a softer acid, binds more strongly to softer donors such as Cl, S and P ligands. Some examples are cited below:

Coordination Number	Geometry	Hybridisation	Example
2	Linear	*sp*	$[Zn(CH_3)_2]$, $[Cd(CH_3)_2]$
4	Tetrahedral	sp^3	$[Zn(NH_3)_4]^{2+}$, $[CdCl_2(R_3P)_2]$, $[ZnCl_2(NH_3)_2]$, $[CdCl_4]^{2-}$, $[Cd(NH_3)_4]^{2+}$, $[ZnCl_2(R_2S)_2]$
5	Square pyramidal	sp^3d	$[Zn(acac)_2.H_2O]$, $[Zn(terpyridyl)\ Cl_2]$
6	Octahedral	sp^3d^2	$[Zn(NH_3)_6{}^{2+}]$

30.5. MERCURY COMPOUNDS

30.5.1. Mercury (I)—Mercury (II) Equilibria. A study of the mercury chemistry is incomplete without an appreciation of the Hg(I)—Hg(II) equilibrila. The redox potentials of the difierent couples are:

$$Hg_2^{2+} + 2e \rightleftharpoons 2Hg \quad ; \quad E^\circ = +\ 0.789 \text{ volts} \quad \ldots(1)$$
$$2Hg^{2+} + 2e \rightleftharpoons Hg_2^{2+} \quad ; \quad E^\circ = +\ 0.920 \text{ volts} \quad \ldots(2)$$
$$Hg^{2+} + 2e \rightleftharpoons Hg \quad ; \quad E^\circ = +\ 0.854 \text{ volts} \quad \ldots(3)$$
$$Hg_2^{2+} \rightleftharpoons Hg + Hg^{2+} \quad ; \quad E^\circ = -\,0.131 \text{ volts} \quad \ldots(4)$$

Only those oxidants with redox potentials within the range + 0.789 to + 0.854 volts can oxidise metallic mercury to the mercurous state. Oxidants with potentials higher than + 0.854 volts will oxidise mercury to the mercuric state. From a practical viewpoint we do not have any oxidant whose potential lies in the range + 0.789 to + 0.854 volts. Hence direct oxidation of mercury to the mercurous state is not possible. The only way of having mercury (I) is to reduce mercury (II) in the presence of metallic mercury according to (4).

Also recall that the equilibrium ratio Hg_2^{2+}/Hg^{2+} in solution is 116 (section 30.2). A mercurous compound for which the mercuric analogue is very sparingly soluble has to disproportionate to mercury and the mercuric compound. Thus mercurous sulphide readily disproportionates to Hg and HgS. Again $Hg(CN)_2$ though soluble is practically undissociated and hence the concentration of Hg^{2+} ions is very very low. As a result mercurous cyanide cannot be prepared. Similarly we find no mercurous hydroxide or oxide. To sum up only those mercurous compounds will survive, which are either very insoluble or whose ionised mercuric analogues are suficiently soluble. Thus mercurous halides, nitrate and the perchlorate are stable and do not disproportionate.

30.5.2. Mercuric Oxide. The compound can be obtained as red crystals by heating the metal at ~ 350°C in oxygen, by pyrolysis of $Hg(NO_3)_2$ or heating an alkaline solution of K_2HgI_4. A yellow form of HgO is obtained on the addition of alkali to a mercuric solution. The red and the yellow forms differ only in particle size. The oxide is weakly basic and dissolves in acids to form mercuric salts. The oxide has a zig-zag chain structure —O—Hg—O—Hg—O—with $< HgOHg = 109°$ and $< OHgO = 179°$. Evidently mercury (II) utilises *sp* hybridisation. The compound finds application as a pigment for painting outer surface of ship bottoms. The poisonous nature of HgO prevents marine growth.

30.5.3. Mercuric Sulphide. It is precipitated as a black material on passing H_2S through a solution of a mercuric salt. Grinding of metallic mercury and sulphur also gives HgS. There is a red form also, which is obtained by subliming the black variety. The stable red variety is a costly pigment. The sulphide is very insoluble ($K_{SP} = 10^{-54}$) and can be brought into solution by boiling with aqua regia.

30.5.4. Mercuric Chloride (Corrosive Sublimate). This is obtained by heating mercury in an atmosphere of chlorine. This is commonly prepared by volatilisation of a dry-mixture of sodium chloride and mercuric sulphate:

$$HgSO_4 + 2NaCl \rightarrow Na_2SO_4 + HgCl_2$$

It is moderately soluble in water, the solubility increasing in the presence of chloride ions owing to the formation of $[HgCl_4]^{2-}$. In sharp contrast to HgF_2 which is ionic, $HgCl_2$ and the other mercury (II) halides are covalent. The two chloride atoms are bonded linearly to mercury (*sp* hybridisation). It is a nonelectrolyte. With reducing agents such as $SnCl_2$ it is first reduced to Hg_2Cl_2 and then to Hg.

Because of its reaction with proteins it is a violent poison. The best antidote is the white of egg which forms with the mercury compound an insoluble coagulum. A dilute solution (1:1000) is used as an antiseptic.

30.5.5. Mercuric Bromide and Mercuric Iodide. These are obtained by the addition of bromide or iodide ions to a solution of mercuric chloride. The solubility of the halides in aqueous solution decreases in the order: $HgF_2 > HgCl_2 > HgBr_2 > HgI_2$. Excess of halide ions leads to the formation of halo complexes such as $[HgI_4]^{2-}$. In aqueous solution both the bromide and the iodide stay as undissociated covalent compounds. Relative to the ionic HgF_2(M.P. 645°C) the other halides have low melting points ($HgCl_2$, 280°C; $HgBr_2$, 238°C and HgI_2, 257°C).

30.5.6. Mercuric Nitrate. This is obtained by the action of excess of nitric acid on metallic mercury:

$$6Hg + 8HNO_3 \rightarrow 3Hg_2(NO_3)_2 + 4H_2O + 2NO$$
$$Hg_2(NO_3)_2 + 8HNO_3 \rightarrow 6Hg(NO_3)_2 + 2NO + 4H_2O$$

This is soluble in water and is an ionic compound of mercury (II). In the absence of acid it hydrolyses to a basic nitrate.

30.5.7. Mercuric Sulphate. This is prepared by heating metallic mercury with sulphuric acid and evaporating to the point of crystallisation:

$$2Hg + 2H_2SO_4 \rightarrow Hg_2SO_4 + SO_2 + 2H_2O$$

This is soluble in water and is stable in presence of acids.

30.5.8. Reactions of Mercury Compounds with Ammonia. The reactions of mercuric chloride with ammonia are complicated and the products and their relative proportions are dependent on conditions:

$$HgCl_2 + 2NH_3 \rightarrow Hg(NH_3)_2Cl_2 \downarrow \quad \ldots (1)$$

$$HgCl_2 + 2NH_3 \rightarrow Hg(NH_2)Cl \downarrow + NH_4Cl \quad \ldots (2)$$

$$2HgCl_2 + 4NH_3 + H_2O \rightarrow Hg_2NCl.H_2O + 3NH_4Cl \quad \ldots (3)$$

In concentrated NH_4Cl solution equation (1) will be favoured and addition of ammonia to $HgCl_2$ will lead to the precipitation of $Hg(NH_3)_2Cl_2$. The precipitation of $Hg(NH_2)Cl$ is favoured in dilute ammonia solution and in the absence of NH_4Cl The compound $Hg_2NCl.H_2O$ cannot be prepared pure by reaction (3). It has been obtained by acidifying *Million's base* ($Hg_2NOH.2H_2O$) with HCl. The Million's base is obtained by the action of aqueous ammonia on yellow HgO:

$$2HgO + NH_4OH \rightarrow Hg_2NOH.2H_2O$$

Salts of Millon's base $Hg_2NX.xH_2O$ ($X = Cl^-, I^-$ etc.) are known. The dichloro diamminemercury (II), $Hg(NH_3)_2Cl_2$, has a tetrahedral structure (*sp*^{3} hybridisation). The infusible white precipitate $HgNH_2Cl$ contains amide links in an infinite chain $-Hg \leftarrow NH_2-Hg \leftarrow NH_2-$. The nitrogen atoms are tetrahedral but the $N-Hg-N$ link is linear and the chlorine lies in between the chains. Mercuric salts of oxyacids do not form such infusible white precipitate with ammonia because mercury does not form a covalent link with the oxygen of their anions.

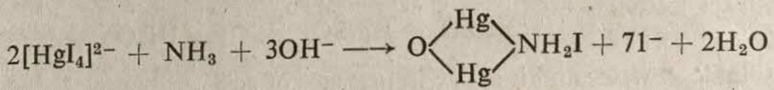
The reactions of Hg_2Cl_2 with ammonia lead to dark residues which contain $HgNH_2.Cl$ and $Hg_2NCl.H_2O$ alongwith metallic mercury. The metallic mercury appears as a consequence of the disproportionation of the initial mercurous compound (say $Cl-Hg-Hg-NH_2$).

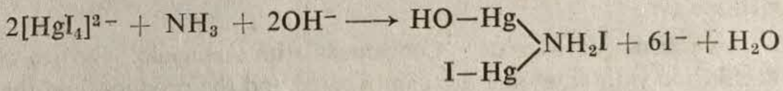
$$Hg_2Cl_2 + 2NH_3 \rightarrow HgNH_2Cl \downarrow + Hg + NH_4Cl$$

Nessler's Reagent and Nessler's Precipitate: Nessler introduced a reagent made up of HgI_2, excess KI and rendered alkaline with caustic alkalies for qualitative detection as also for quantitative estimation of ammonia. It has been shown that Nessler's reagent is formed out of the reaction:

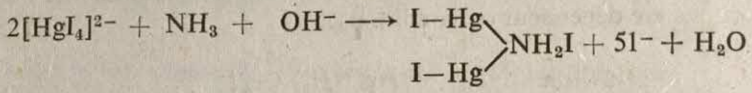
$$[HgI_4]^{2-} + 2OH^- \rightleftharpoons [Hg(OH)_2I_2]^{2-} + 2I^-$$

Nessler's reagent produces a characteristic brown precipitate with ammonia. However the colour varies from brown to deep brown to chocolate as also the composition depending on the concentrations of $[HgI_4]^{2-}$ and OH^- ions as well as on the amount of ammonia added:





$$2[HgI_4]^{2-} + NH_3 + 2OH^- \longrightarrow \begin{matrix} HO-Hg \\ I-Hg \end{matrix} \rangle NH_2I + 6I^- + H_2O$$



$$2[HgI_4]^{2-} + NH_3 + OH^- \longrightarrow \begin{matrix} I-Hg \\ I-Hg \end{matrix} \rangle NH_2I + 5I^- + H_2O$$

As the concentration of ammonia or iodomercury (II) ion increases the precipitate tends towards the formula $NH_2Hg_2I_3$. When OH^- concentration increases and the other reactants are constant the formula of the precipitate approaches OHg_2NH_2I.

30.5.9. Mercurous Chloride (Calomel). On a commercial scale this is made by subliming a mixture of $HgCl_2$ and Hg. It can be readily obtained as a white precipitate by adding a soluble chloride to a solution of mercurous nitrate. When treated with ammonia it gives a dark precipitate containing metallic mercury and $HgNH_2Cl$. This is used in the making of standard calomel electrode.

30.5.10. Mercurous Nitrate. This is prepared by the action of warm dilute nitric acid on excess of mercury:

$$6Hg + 8HNO_3 \rightarrow 3Hg_2(NO_3)_2 + 4H_2O + 2NO$$

In presence of water it undergoes hydrolysis to $Hg_2(OH)NO_3$. With chloride ion a precipitate of Hg_2Cl_2 is obtained. When heated dry the compound decomposes to give HgO.

30.5.11. Mercurous Sulphate. This is obtained by the action of sulphuric acid on an excess of mercury:

$$2Hg + 2H_2SO_4 \rightarrow Hg_2SO_4 + 2H_2O + SO_2$$

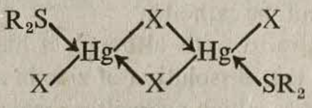
This is sparingly soluble in water and hence can be obtained by adding a soluble sulphate to mercurous nitrate. This is used in Weston standard cell.

30.5.12. Mercury Complexes. From an appreciation of the overall charge on the mercurous and the mercuric mercury we would not expect their complexation tendency to be much different. But if we recognise one positive charge concentrated on each mercury (as Hg^+-Hg^+) we would expect mercurous mercury to have much smaller complexation tendency. Add to this the ready disproportionation of many mercurous compounds to mercury (II) and mercury. The overall result is that Hg_2^{2+} has little tendency to complexation. Mercurous complexes occur only for those ligands for which the mercuric complexes are not strong. Such ligands are oxalate, succinate etc.

The mercuric ion has a moderately strong tendency to complexation. Some examples are given below:

Coordination Number	Geometry	Hybridisation	Example
2	Linear	*sp*	HgX_2
4	Tetrahedral	sp^3	$[HgX_4]^{2-}$, $Hg(NH_3)_2X_2$ $HgCl_2(Ph_3AsO)_2$, $(HgX_2.R_2S)_2$
6	Octahedral	sp^3d^2	$[Hg(en)_3]^{2+}$

The complex $HgX_2.R_2S$ attains four-coordinated tetrahedral stereochemistry with halogen bridges:



As remarked earlier mercury (II) has a pronounced preference for large polarisable soft donors. The most stable complexes are those with halogen, nitrogen, phosphorus and sulphur as ligand atoms. The order of increasing stability of the halide complexes is $Cl^- < Br^- < I^-$ with little tendency to form fluoride complexes.

30.6. ISOLATION OF THE GROUP IIB ELEMENTS

30.6.1. Zinc. The best known ores of industrial importance are *zinc blende* (ZnS) and *calamine* ($ZnCO_3$). *Franklinite* ($ZnO.Fe_2O_3$) and *willemite* (Zn_2SiO_4) are of minor importance. Most zinc ores need to be pulversised and concentrated by floatation process.

The ores are then roasted in a current of air or calcined to the oxide form:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2 \;;\; ZnCO_3 \rightarrow ZnO + CO_2$$

The roasting of the sulphide ore is carried out in a rotary shelf burner which is provided with horizontal shelves and air-cooled raking arms. The ore is added at the top and zinc oxide is discharged at the bottom.

Three methods are in vogue for the reducation of the oxide to the metal. The first and the commonest is the retort process, where the zinc oxide is reduced by heating with carbon in retorts. An intimate mixture of zinc oxide and coal is placed in cylindrical earthen ware retorts (8 inch internal diameter and 5ft in length). The retorts are connected to air-cooled earthenware condensers. A large number of retorts are placed in tiers in a large furnace and heated to 1100°C.

$$ZnO + C \rightarrow Zn + CO \;;\; ZnO + CO \rightleftharpoons Zn + CO_2$$

At high temperature the reduced zinc reacts with CO_2 to go back to the oxide stage. Hence an excess of coal is always maintained to prevent build-up of any appreciable concentration of CO_2. Similarly since zinc reacts at high temperature with oxygen to give zinc oxide, air must be excluded from the retorts. Eventually zinc distills and is collected in the earthenware condensers. This zinc is known as *spelter* and contains some impurities such as cadmium and lead.

The second method consists in heating a mixture of zinc oxide and coke in an electric arc furnace (at 1200°C). The furnace is lined up with refractory material with electrodes located near the top and bottom. The charge is introduced at the top and the spent material taken off at the bottom. Zinc vapour and CO escape at the top and the metal condensed in earthenware vessels.

The third method involves dissolution of the roasted ore in dilute H_2SO_4 followed by electrolysis. The zinc sulphate solution however needs to be purified prior to electrolysis. This is done by adding iron to remove any arsenic and antimony. The iron is then oxidised by MnO_2 to the ferric state which is then precipitated by adding ZnO. Finally metallic zinc is added to precipitate less electropositive metals like copper, cobalt etc. The purified solution is electrolysed when pure zinc is deposited on the cathode.

Pure zinc is not responsive to acids although it has a substantially negative standard potential. In order that dissolution of zinc in acids is possible evolution of H_2 is necessary. But zinc has a high overvoltage which means that the reaction $H + H \rightarrow H_2$ on a pure zinc surface is very slow. But when the zinc is impure, that is when it contains impurities such as copper, nickel, etc with low overvoltage hydrogen can readily liberate from the surfaces of these metals. Thus zinc readily passes into solution. Zinc also dissolves in moderately concentrated solution of alkalies with liberation of hydrogen and formation of zincates.

30.6.2. Cadmium. Cadmium invariably occurs as an impurity in zinc ores usually as 1 part in 200 parts of zinc. The metal is recovered as a by-product of the zinc extraction. Since the two elements have reasonably different boiling points they can be separated by fractional distillation. Since zinc is more electropositive, cadmium may also be precipitated from a cadmium (II) solution by metallic zinc:

$$Cd^{2+} + Zn \rightarrow Cd + Zn^{2+}$$

The difference in the standard potentials also indicates that by regulating the potential during electrolysis of an impure zinc sulphate solution pure cadmium may be deposited on the cathode before any zinc.

30.6.3. Mercury. The chief source of the metal is *cinnabar* (HgS). The ore is roasted and the evolved vapour of mercury and SO_2 are led through tortuous flues where the metal condenses:

$$HgS + O_2 \rightarrow Hg + SO_2$$

Commercial mercury is impure, being contaminated with more basic elements such as copper, zinc etc. It may be purified by dropping a thin stream of impure mercury through a column of dilute nitric acid. Some mercurous nitrate is produced which reacts with baser metals producing their nitrates and liberating mercury. The process should be repeated several times to obtain mercury of the desired purity level. A better and more widely used technique is distillation of impure mercury under vacuum.

30.7. USES OF THE GROUP IIB ELEMENTS

Zinc: One important use of zinc is as a protective coating for iron. Zinc readily forms a coating of basic carbonate in contact with air, which coating protects the iron. Zinc being more electropositive releases electrons to the corroding agent (atmospheric oxygen or moisture) and thus protects iron at the cost of its own oxidation. Iron thus protected is called *galvanised iron*. The iron material is washed in dilute acid to remove any oxide film and is then immersed in fused zinc. This can also be accomplished by depositing zinc on the iron cathodes via electrolysis. Galvanised iron is used in corrugated iron sheet, pipe, bath tub etc. Zinc is also an important constituent of alloys called *brasses*. These are composed mainly of copper and zinc with minor quantities of other metals. The brass alloys are generally stronger, more ductile, cheaper and are easily processed through machines than is copper alone. Brasses are used as tubing, valves, cartridge cases, utensils etc.

Zinc Plating: Zinc may be deposited as a protective coating on iron and steel surfaces by hot dipping in fused zinc (*glavanising*), by *sheradising* (in which the article is heated to ~ 370°C in zinc dust) or by *electroplating*. Because of the significant negative standard potential of the Zn^{2+}/Zn couple ($E^\circ = -0.763$ volts) it would not be favoured over discharge of hydrogen (H^+/H; $E^\circ = 0.00$ volts; at pH 7, $E^\circ = -0.41$ volts) at the cathode. Fortunately zinc has a high hydrogen overvoltage so that once there is some zinc on the cathode surface electrolysis runs in favour of deposition of zinc. Most zinc plating is done from acid or from cyanide solution. Acid bath constitutes zinc sulphate, ammonium chloride, sodium acetate buffer and very little H_2SO_4. The anodes are cast zinc of 99% purity. Too much acid is to be avoided as in that case zinc dissolves not only anodically but also chemically.

Cadmium: This also serves as a protective coating on iron and steel. The metal is usually deposited electrolytically. Cadmium alloys (99% Cd, 1% Ni; 98.7% Cd, 0.7% Ag, 0.6% Cu) are used in aircarft engines. Sponge cadmium is used as anode in the Ni—Cd alkali storage batteries. Cadmium rods are used in atomic reactors to absorb neutrons.

Mercury: It is used for filling thermometers, barometers and high vacuum pumps. As amalgams it finds use in many laboratory reduction reactions. It also serves in the mercury vapour lamps. The metal also serves as electrode in many laboratory and industrial electrolyses.

30.8. ANALYTICAL REACTIONS OF THE GROUP IIB ELEMENTS

Zinc: This element is included in Group IIIB of the qualitative scheme of analysis. Its sulphide has a solubility product $K_{SP} \sim 10^{-23}$ and thus the metal is precipitated as sulphide in weakly acid medium and in ammoniacal mediu alongwith those of cobalt, nickel and manganese. It is finally detected as the insoluble ferrocyanide $Zn_3K_2[Fe(CN)_6]_2$. For quantitative estimation zinc is precipitated as zinc ammonium phosphate at pH ~ 6.6 and dried (105°C) and weighed as $ZnNH_4PO_4$. Else the precipitate is ignited to $Zn_2P_2O_7$ at 800–900°C and weighed. Zinc can also be precipitated from dilute acetic acid or slightly ammoniacal solution with quinaldinic acid (QH) and weighed as $ZnQ_2.H_2O$.

Cadmium: This is included in Group IIA of the qualitative scheme and is precipitated from dilute acid solution as sulphide. In ammoniacal medium copper and cadmium remain in solution as ammine complexes. Copper is then treated with excess KCN whereby stable cuprocyanide complex and less stable cadmicyanide are formed. The cadmicyanide complex formed dissociates to an extent which is enough to exceed the solubility product of CdS when the solution is treated with H_2S. Thus a yellow precipitate indicates cadmium. Several noncyanide detections of copper and cadmium have been proposed. One method precipitates cadmium with N-benzoyl-N-phenylhydroxylamine (RH) from ammoniacal solution as CdR_2. In the filtrate copper may be detected as the rose-red insoluble $[Cu(BigH)_2]SO_4$ by the addition of biguanide sulphate.

Mercury: Mercurous mercury gives an insoluble chloride and hence it is included in Group I of the qualitative scheme. It is confirmed by the addition of dilute ammonia to the Hg_2Cl_2 precipitate, when a black material is obtained. This black material is a mixture of Hg and $NH_2-Hg-Cl$.

Mercuric mercury gives a highly insoluble sulphide (K_{SP} of HgS, $\sim 10^{-54}$) and thus belongs to Group IIA of the qualitative scheme. HgS is dissolved in aqua regia, the solution taken to dryness and then the mass is dissolved in water. On addition of $SnCl_2$ a white precipitate of Hg_2Cl_2 separates, which turns grey on standing. Mercury can be estimated gravimetrically as HgS. It has also been quantitatively precipitated at pH 6-7 with 2(*o*-hydroxyphenyl) benzimidazole (RH). The precipitate is dried at 130-140°C and weighed as HgR_2.

STUDY QUESTIONS

1. Give the electronic configurations of Group IIB elements. Discuss on this basis their properties and show that we cannot regard these elements as transition elements.
2. Suggest methods whereby it can be shown experimentally that mercurous compounds have the formula Hg_2X_2 and not HgX.
3. Give a comparative assessment of the Group IIA and IIB elements.
4. How is mercury extracted from its chief ore and how is it purified? How may the following be prepared from mercury—mercurous nitrate, mercuric nitrate, mercurous chloride and mercuric chloride?
5. Zinc has a substantially negative standard electrode potential, yet pure zinc does not easily liberate hydrogen from acids. How do you explain this?
6. Mercury is very peculiar among metals. Discuss.

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31

Thorium and Uranium

In this Chapter we briefly discuss two naturally occurring actinides, namely thorium and uranium. Both the elements are radioactive. Thorium-232 and uranium-238 are both alpha emitters with long life, 1.34×10^{10} years and 4.5×10^{9} years respectively. Prior to the discovery and study of the actinides thorium used to be included in Group IVA alongwith titanium, zirconium, and hafnium. This particular classification was justified in view of thorium behaving as a straightforward quadrivalent element. Uranium used to be included in Group VIA alongwith chromium, molybdenum and tungsten because of its dominating hexavalence. The relative abundances of the elements are: Th (0.0012%); U(0.0004%).

31.1. THORIUM

31.1.1. General Remarks. Its atomic number is 90 and electronic configuration is $[Rn]6d^2 7s^2$. All the four electrons in the d and s orbitals are utilised in compound formation. The thorium ion Th^{4+} has a radius 0.99A which is substantially bigger than those of Zr^{4+} and Hf^{4+} (0.81A). Although the charge on the ion is large the size is also substantial. Therefore on an average we find that the chemistry of thorium is in many cases that of an M^{4+} cation and in several other cases that of a covalent $-\overset{|}{\underset{|}{M}}-$. Fajans' rules would predict that the element should have a strong tendency to complexation.

Some important physical data are: M.P. 1750°C; B.P. 4200°C; density (gm/ml), 11.7.

Thorium Oxide and Hydroxide: The hydroxide is precipitated as a gel from solutions of its salts on the addition of alkali. Thorium hydroxide is not soluble in alkali solution, which behaviour shows only a basic character in the hydroxide. It dissolves in alkali carbonates however due to the formation of carbonato-complex (eg: $M_2^1[Th(CO_3)_3]$). Like strong bases the hydroxide absorbs CO_2

from the air. The dioxide is made by heating the hydroxide strongly in air. It is a refractory solid (M.P. 3220°C).

Halides: All the tetrahalides are known. The anhydrous halides are made by the interaction of the metal and the halogen, or by the action of the halogen on a mixture of ThO_2 and carbon. The hydrated halides can be made by the action of halic acids on $Th(OH)_4$. The tetrahalides are crystalline solids and the behaviour of the fluoride is that of a salt. Even the tetrachloride gives a conducting solution in fused state. With the exception of the fluoride, the other halides can be sublimed in vacuum at 600–700°C.

Oxyacid Salt: Thorium forms a very soluble nitrate ($Th(NO_3)_4.5H_2O$), and sulphate, chlorate, bromate, etc. Many of these, particularly the sulphate, can form several hydrates. The oxalate, iodate and the phosphate are precipitated even from 6*M* acid solutions and in this respect thorium differs from the lanthanides. This difference in solubility is made use of in its separation from the lanthanides.

Complexes: The Th^{4+} ion being quite basic its trend to form oxo compounds like Zr (IV) and Hf (IV) is poor. The Th^{4+} ion is more difficult to hydrolyse, although above pH 3-4 some hydroxy species have been postulated. Thus in perchlorate solution several ions $Th(OH)^{3+}$, $Th(OH)_2^{2+}$, $Th_2(OH)_2^{6+}$, etc. seem to exist.

In its complexes coordination numbers 6, and sometimes 8 are encountered. Some examples are: $M_2[Th(NO_3)_6]$, $M_2[ThF_6]$, $K_4[Th(Ox)_4]$, $[Th(EDTA).2H_2O]$, $[Th(acac)_4]$, etc. Some of these complexes are hydrolysed by water. Taking the valence bond model for 6 coordinated (d^2sp^3) or 8 coordinated (d^4sp^3) thorium (IV) ($6d^0$), there still remains *d*-orbital to facilitate nucleophilic attack by H_2O molecules.

31.1.2. Isolation of Thorium. Thorium-rich ores such as *thorianite* ($ThO_2 + UO_2$) and *thorite* ($ThSiO_4$) are scarce. The major workable source of thorium is *monazite* sand available in Kerala (India) and in Brazil. Monazite is essentially a complex phosphate of some lanthanides being contaminated with silica. The ore also contains varying amounts of uranium. Concentration of the monazite sand leads to fractions which contain ~ 10% ThO_2.

There are two current processes for working up of the ore. According to one procedure the ore is opened up with hot H_2SO_4 which dissolves the thorium and the rare earths. In the other process monazite is digested with ~45% NaOH solution at ~140°C which yields insoluble ThO_2 and the lanthanide oxides. The phosphate is recovered in the filtrate as sodium phosphate.

Separation of thorium from the lanthanides and uranium can be achieved by a variety of methods. In this respect the sparing solubility of many salts and double salts of thorium is made use of. Thus from the above sulphuric acid leach double sulphate of thorium and sodium can be crystallised. Thorium can also be precipitated as the oxalate or the iodate. The iodate, in particular, effects excellent separation of thorium from the lanthanides. The oxalate or the iodate can then be calcined to give ThO_2, which is contaminated with uranium oxide. Finally thorium can be recovered as crude thorium nitrate pentahydrate. Thorium can further be purified by solvent extraction as described below.

In the second process the insoluble oxides of Th, U and the lanthanides are dissolved in ~35% HCl at 80°C. The filtrate is brought to pH ~6.0 when thorium and uranium hydroxides separate, which are contaminated with little lanthanide hydroxides. The crude hydroxide is dissolved in nitric acid and the solution extracted with organic solvents such as tributyl phosphate (TBP) when thorium and uranium move into the organic phase leaving the lanthanides in the aqueous phase. Thorium and uranium are then separated by selective stripping of the organic phase with aqueous nitric acid.

ThO_2 is not reduced by hydrogen nor by carbon. $ThCl_4$ may be reacted with sodium at 525°C. Electrolysis of $ThCl_4$ in a bath of fused NaCl plus KCl has also been carried out. An electrolyte containing equal parts by weight of NaCl and KCl alongwith the double fluoride $ThF_4.KF$ has also been found suitable. A carbon crucible serves as the anode and a molybdenum rod as cathode. At the end of the electrolysis the cathode is slowly raised. The electrolyte solidifies and protects the thorium powder against oxidation. The deposit is stripped, leached with water and dried. Very pure thorium may be obtained by the van Arkel-de Boer process. The crude metal powder is converted, by heating it in iodine vapour to volatile ThI_4. The ThI_4 is then thermally decomposed on a hot filament maintained at ~1200°C. The iodine then combines with more of crude thorium and the process becomes self sustained.

31.1.3. Uses of Thorium. The major applications of thorium are three fold: in nuclear power generation, in magnesium alloys and in gas mantles industry. Thorium is a source for atomic power. Thorium-232 by neutron capture and via subsequent beta emission becomes uranium-233 which is fissionable:

$$\begin{array}{l} {}^{232}_{90}\text{Th} + {}^{1}_{0}n \rightarrow {}^{233}_{90}\text{Th} \rightarrow {}^{233}_{91}\text{Pa} + {}^{0}_{-1}e \\ \qquad\qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\qquad\quad\; {}^{233}_{92}\text{U} + {}^{0}_{-1}e \end{array}$$

Uranium-233 can function in a fission chain reaction as can U-235 or Pu-239, and thus Th-232 has the potentiality of generating power. The interest in the application of thorium for this purpose is due to its greater abundance over uranium. However it has disadvantages also since there occurs a side reaction whereby U-233 by (n, $2n$) process gives non-fissionable U-232:

$${}^{233}_{92}\text{U} + {}^{1}_{0}n \rightarrow {}^{232}_{92}\text{U} + 2\,{}^{1}_{0}n$$

Incorporation of 3% thorium into magnesium gives light weight alloys that are exceptionally suitable for airplane and missile construction.

In 1884 use of thorium oxide was patented for the manufacture of the incandescent mantle—a lattice structure consisting of a mixture of thorium oxide and 1% cerium oxide. With the advent and popularity of electricity the use of gas mantles decreased but is still used in portable gas lights. It is also used (about 1% ThO_2)

in tungstic acid prior to its reduction to the metal for subsequent use as tungsten filament lamp. Incorporation of thorium increases the life of tungsten filaments.

31.1.4. Analytical Reactions of Thorium. Thorium (IV) is precipitated as the hydroxide in group IIIA. This is insoluble in excess alkali and hence comes along-with ferric oxide, TiO_2, etc. The precipitate is dissolved in dilute HCl, boiled and treated with oxalic acid solution when a white precipitate of $Th(Ox)_2$ appears. Cerium is also precipitated as oxalate. The precipitate is separated and treated with excess oxalate when the thorium oxalate dissolves due to the formation of $K_4[Th(Ox)_4]$.

For quantitative estimation the thorium oxalate can be precipitated from ~3.5% HCl solution, collected and ignited to ThO_2. Thorium can also be precipitated as thorium sebacate from a faintly acid solution by the addition of sebacic acid $HOOC(CH_2)_8COOH$ and the precipitate $[Th.\ (OOC(CH_2)_8COO)_2]$ ignited to ThO_2. Many organic precipitating reagents are now available for direct estimation of thorium without igniting to ThO_2.

31.2. URANIUM

31.2.1. General Remarks. Uranium is one of the naturally occurring actinides. Of the actinides the chemistry of uranium is well understood. The following valences of uranium are known: $+6$, $+5$, $+4$, $+3$. Of these the hexavalent state is the prominent valence—so much so that prior to our knowledge of the actinides as a family, uranium used to be included in group VI after molybdenum and tungsten.

Its atomic number is 92 and the electronic configuration is $[Rn]5f^3d^17s^2$ so that it has six electrons outside the stable radon core. Some important physical data are: M. P., 1132°C; B.P., 3813°C; density (gm/ml), 19.1; M^{3+} radius, 1.03A; M^{4+} radius, 0.93A.

In the $+6$ state the compounds tend to be covalent. This is shown by the volatility of UF_6 (M.P. 64°C). Incidentally this is the most readily available volatile uranium compound and has been utilised in the separation of the isotopes of mass number 235 and 238. In this high valence state the element has (like Mo and W) a flair of forming large number of dioxouranium (UO_2^{2+}) salts and complexes. The oxide UO_3 is not entirely acidic, rather it is amphoteric. It forms salts with acids (eg:UO_2Cl_2) and uranates with alkalies $M_2U_2O_7$.

In the $+4$ state $U(OH)_4$ has practically no acid properties. Thus it reacts with acids to give uranium (IV) salts such as UX_4. The uranium (IV) halides are crystalline solids and possess much higher melting points compared to those of uranium (VI). We have noted earlier, for example, with V, Mo or W, that with decrease in valence the trend of forming oxo salts and oxo complexes falls. This is true with uranium (IV) as well. All its complexes are of the non-oxo types eg: $M_2[UCl_6]$, $[NH_4]_4[U(Ox)_4]$ etc.

Uranium (V) is very unstable and has a strong tendency to disproportionate: $2U(V) \rightarrow U(VI) + U(IV)$. It forms oxo- as also non-oxo-compounds.

31.2.2. Hexavalent Uranium. This is the common and stable oxidation state or uranium. Uranium hexafluoride is obtained by the action of fluorine on uranium in the presence of little chlorine acting as a catalyst. In the absence of chlorine the reaction may not proceed beyond UF_4 stage. It forms volatile (M.P. 64°C) yellow crystals. It is very hygroscopic, fumes in moist air and is instantly hydrolysed by water to UO_2F_2. The black hexachloride, UCl_6, has been obtained by the disproportionation of UCl_5 in vacuum:

$$2UCl_5 \xrightarrow{\text{vacuum } (120\text{–}150^\circ C)} UCl_4 + UCl_6$$

The two products are separated by making use of their difference in volatility.

The hexafluoride is a strong fluorinating agent, thus CS_2 is converted to SF_6. Incidentally enrichment of U-235 isotope has been achieved through gaseous diffusion of UF_6.

Uranium trioxide is obtained by careful heating of $UO_2(NO_3)_2$ or $(NH_4)_2U_2O_7$:

$$\begin{tikzcd}
(NH_4)_2U_2O_7 \arrow[r, "250^\circ C"] & 2UO_3 + H_2O + 2NH_3 \arrow[dl, "400^\circ C", "+C"'] \arrow[d, "700^\circ C"] \\
UO_2 & U_3O_8
\end{tikzcd}$$

The oxide is amphoteric, dissolving in acids to form uranyl salts UO_2X_2 and giving uranates with metallic oxides or carbonates: $2UO_3 + Na_2O \rightarrow Na_2U_2O_7$. Uranyl chloride is obtained by the dissolution of UO_3 in aqueous HCl whereby $UO_2Cl_2 \cdot 3H_2O$ is obtained as yellow crystals. The anhydrous compound is obtained by the action of chlorine on UO_3. Uranyl nitrate is obtained by dissolving UO_3 or U_3O_8 in nitric acid, and uranyl sulphate by evaporating a solution of $UO_2(NO_3)_2$ in H_2SO_4.

Uranyl nitrate is readily extracted into many organic solvents such as TBP, alcohols, ketones etc. The property is made use of in its extraction from ores, and also in its separation from other fission products.

Uranyl ion, by virtue of its high charge, has a strong tendency to complexation. Complexes obtained are of dioxouranium (VI). Some examples are: $UO_2(NO_3)_2 \cdot 2B (B = NH_3, py)$; $[UO_2(acac)_2]$; $[UO_2(oxin)_2]$ oxinH, etc. All uranium (VI) compounds are coloured yellow or greenish yellow and are diamagnetic.

Aqueous solutions of uranyl salts give an acid reaction due to hydrolysis. Some of the hydrolysed and polymerised species are UO_2OH^+, $(UO_2)_2(OH)_2^{2+}$, etc. the exact species depending on the medium. In presence of sulphate ions a complex $UO_2(SO_4)_2^{2-}$ is formed. In presence of phosphate ions complexes like $UO_2H_2PO_4^+$, $UO_2H_2PO_2^{2+}$, etc. are formed.

31.2.3. Pentavalent Uranium. Uranium (V) has a strong tendency to disproportionate: $2U(V) \rightarrow U(IV) + U(VI)$. It is also oxidised with great ease and rapidity to uranium (VI). The ground state electronic configuration of uranium (V) is $[Rn]5f^1$. Most of the uranium (V) compounds may be considered to contain covalently bound uranium (V), some being of the following oxotypes: UO_3^-,

UO_4^{3-}, UO_2^+ and UO^{3+}. The uranium pentachloride is obtained by chlorination of UCl_4. Since the pentachloride easily disproportionates, it is recovered by cooling of the reaction product.

$$2UCl_4 + Cl_2 \xrightarrow{520-550°C} 2UCl_5;2UCl_5 \xrightarrow{\text{vacuum}(120-150°C)} UCl_4 + UCl_6$$

A number of salts of the anion $[UCl_6]^-$ have been prepared by the oxidation of $[UCl_6]^{2-}$ by chlorine in intromethane. The salts isolated include $Cs[UCl_6]$, $Me_4N[UCl_6]$, $Ph_4N[UCl_6]$ etc. Some adducts of the type $UX_5.L$ (X = Cl, Br ; $L = OPPh_3$) are also known. The largest group of uranium (V) compounds are the alkoxide and halide alkoxides:

$$UCl_4 + 4NaOR \rightarrow U(OR)_4 \xrightarrow[NaOR]{O_2} U(OR)_5$$

$$U(OEt)_4 + \tfrac{1}{2}Br_2 \rightarrow U(OEt)_4Br \xrightarrow{NaOEt} U(OEt)_5 + NaBr$$

$$UCl_5 + 5ROH + 5NH_3 \rightarrow U(OR)_5 + 5NH_4Cl$$

$$U(OEt)_5 + 5ROH \rightarrow 5EtOH + U(OR)_5$$

Uranium (V) oxotrichloride has been obtained as shown below:

$$UO_2Cl_2 + MoOCl_3 \rightarrow UOCl_3 + MoO_2Cl_2$$

The green salt $(pyH)_2[UOCl_5]$ is obtained by treating $UCl_4.SOCl_2$ with pyridine in ethanol.

Magnetic behaviour of uranium (V) compounds is mostly consistent with an expected $5f^1$ ground state, although moments are sometimes lower than 1.73 B.M. (cf: UCl_5, 1.42 B.M.; $UCl_5.SOCl_2$, 1.29 B.M.; $Cs[UCl_6]$, 1.71 B.M.; $UCl_5.OPPh_3$, 2.1 B.M.; $NH_4[UF_6]$. 1.74 B.M.).

31.2.4. Quadrivalent Uranium. On moving from + 6 state to the +4 state the acidic properties have practically disappeared. The dioxide is obtained by the reduction of UO_3 or U_3O_8 with hydrogen or carbon. It is a high melting (2176°C) brown solid. The oxide has entirely basic properties. The tetrahalides are generally made by the action of the halogens on uranium, or by the action of the halogens on a mixture of U_3O_8 and carbon. The halides are all high melting solids (UF_4, 1000°C; UCl_4, 567°C; UI_4, 500°C). In fused state these conduct electric current, and hence these have good degree of ionic character.

Acid solution of uranyl salts can be reduced to green U^{4+} by $SnCl_2$ or zinc amalgam. But the U^{4+} tends to be readily oxidised. The acetate and the oxalate are reasonably stable when dry. Uranium (IV) acetate is obtained as light green precipitate by the reduction of uranyl acetate by amalgamated zinc in glacial acetic acid:

$$UO_2(Ac)_2 + Zn + 4HAc \rightarrow Zn[U(Ac)_6] + 2H_2O$$

$$Zn[U(Ac)_6] + 2HCl \rightarrow U(Ac)_4 + ZnCl_2 + 2HAc$$

The liberated water is removed by acetic anhydride.

Hexachloro complexes of uranium (IV) have been obtained by the reduction of uranyl chloride in presence of HCl, and the complex isolated as pyridinium or dipyridyl cation: $(pyH)_2[UCl_6]$, $dipyH_2[UCl_6]$ etc. These form green crystals and are paramagnetic (~ 2.8 B.M.) as expected for a $5f^2$ system. The insoluble oxalate of uranium (IV), $U(Ox)_2$, is very soluble in alkali oxalate solution due to the formation of a soluble complex $K_4[U(Ox)_4]$.

31.2.5. Trivalent Uranium. This oxidation state is mostly known in the trihalides. When UF_4 is heated in H_2, HF is given off and a red-brown solid UF_3 is obtained. UCl_3 is obtained by reducing the tetrachloride with hydrogen. It forms dark red needles, scarcely volatile but hygroscopic. It dissolves in water to a purple-red liquid, which evolves hydrogen, turns green and deposits $U(OH)_4$. The tribromide has also been obtained by the action of hydrogen on UBr_4.

31.2.6. Isolation of Uranium. Major uranium sources are *carnotite* ($2K(UO_2)VO_4.3H_2O$), *pitchblende* (essentially U_3O_8), *uraninite* (UO_2 with UO_3). The ore is first concentrated by hydrometallurgical methods leading to a material with 70–90% U_3O_8 content. Acid treatment now converts uranium to soluble uranyl salt. The uranium may also be precipitated as yellow $(NH_4)_2U_2O_7$ by the addition of ammonia. Generally however uranium is brought to solution as $UO_2(NO_3)_2$ by dissolving the concentrated ore in nitric acid. Uranyl nitrate is soluble in a number of organic solvents such as ether, methyl isobutyl ketone, tributyl phosphate etc. The uranyl nitrate is extracted into one such solvent and the organic layer separated. The uranyl nitrate is then reextracted into an aqueous phase. The solution on evaporation gives uranyl nitrate hexahydrate. This is then thermally decomposed to give UO_3. This is converted by HF to UF_4 which is then further treated with fluorine to give UF_6. This UF_6 is then fed into gaseous diffusion plants where separation of $^{235}UF_6$ from $^{238}UF_6$ takes place.

Metallic uranium is difficult to obtain because of the metal's trend to react with oxygen, halogen, nitrogen and carbon. The metal also reacts with hydrogen at 250–300°C to give a black powder UH_3, which however decomposes at higher temperature to give a very reactive form of finely divided metal. The preferred method for obtaining uranium metal involves reduction of UF_4 or UCl_4 by magnesium turnings when the fused magnesium halide permits the dense uranium metal to settle:

$$UF_4 + 2Mg \rightarrow U + 2MgF_2$$

Electrolysis of UF_4 in a fused 4:1 $CaCl_2$: NaCl bath at 900°C has also been used. The metal is deposited as a powder on a molybdenum cathode and the adhering electrolyte is removed by leaching. High purity uranium has been obtained by the van Arkel-de Boer method.

31.2.7. Uses of Uranium. Uranium has played a lead role in the development of the early science of radioactivity. Prior to the discovery of nuclear fission reactions the utility of uranium was confined mostly to its use in colouring glass and ceramics, and its ores were tapped mainly for radium. But with the knowledge of nuclear fission—the breaking up of the uranium nucleus into fragments of similar size and thus making the lost mass a source of power—the importance of uranium has enormously increased. During nuclear fission some extra neutrous are liberated which can initiate further nuclear chain reaction. In order that the ejected neutron may not escape the uranium metal but may sustain the chain reaction the uranium must have a critical size. U-235 has a small critical mass which is only a few (~ 20) pounds.

Natural uranium has 0.72% U-235 and 99.27% U-238. Separation of U-235 from U-238 becomes essential for fission reactions:

$$ {}^{235}_{92}\mathrm{U} + {}^{1}_{0}n \rightarrow {}^{137}_{56}\mathrm{Ba} + {}^{96}_{36}\mathrm{Kr} + 3\,{}^{1}_{0}n + \text{energy} $$

With the use of moderators such as carbon, heavy water etc. the reaction can be controlled to generate power. U-238 under the same condition captures neutrons and gives rise to plutonium:

$$ {}^{238}_{92}\mathrm{U} + {}^{1}_{0}n \rightarrow {}^{239}_{92}\mathrm{U} + \gamma \rightarrow {}^{239}_{93}\mathrm{Np} + {}^{0}_{-1}e $$

$$ \downarrow $$

$$ {}^{239}_{94}\mathrm{Pu} + {}^{0}_{-1}e $$

Plutonium-239 can undergo fission reaction. Hence U-238 is also used as a nuclear fuel. After irradiation, the fissionable material is separated by dissolving the uranium in nitric acid, and separation of uranium and plutonium is achieved by partition between aqueous and organic phases.

31.2.8. Analytical Reactions of Uranium. The insolubility of $(NH_4)_2U_2O_7$ leads to the inclusion of uranyl uranium in group III of the qualitative scheme. The precipitate of the ammonium diuranate is readily soluble in ammonium carbonate due to the formation of $(NH_4)_4[UO_2(CO_3)_3]$. Upon acidification with HCl and addition of ferrocyanide a brown precipitate of $(UO_2)_2[Fe(CN)_6]$ separates.

A uranium salt may be estimated volumetrically by reducing an acid solution with zinc and titrating the green uranium (IV) with permanganate:

$$ 2KMnO_4 + 5U(SO_4)_2 + 2H_2O \rightarrow 2KHSO_4 + 2MnSO_4 + H_2SO_4 + 5UO_2SO_4 $$

Gravimetrically uranyl salts can be precipitated as $(NH_4)_2U_2O_7$ and then ignited to U_3O_8 and weighed. Uranyl uranium may also be precipitated from dilute acetic acid solution as $UO_2(\text{oxin})_2.\text{oxinH}$ and weighed as such at 105°C or ignited to U_3O_8.

STUDY QUESTIONS

1. Discuss the extraction of thorium and uranium from their ores and enumerate their uses.

2. Previous to our recognition of the actinide family of elements thorium and uranium were included in the Groups IVA and VIA respectively. Discuss the basis of such classification.

3. Comment on the following melting points (°C):

UCl_3	UCl_4	UCl_5	UCl_6
835	590	(327)	179 (decompose)
UF_3	UF_4	UF_5	UF_6
1140 (decompose)	960	<400 (decompose)	64

4. Both Mg^{2+} and UO_2^{2+} are bipositive cations. How would you expect their general chemistry to vary?

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Appendices

Appendix I

Schrödinger Equation and Shapes of Atomic Orbitals

Light waves conform to an equation of the type:

$$\Psi(\mathrm{x}, t) = \mathrm{A}e^{2\pi i \frac{x}{\lambda}} . e^{-2\pi i v t} \qquad \ldots (1)$$

where Ψ is the wave amplitude, commonly called the wave function, A is a constant, x is the distance travelled in the direction of the wave motion, λ wave length, v the frequency and t, the time. The wave equation thus consists of a space dependent part and a time dependent part. If we consider stationary systems, that is, for which the energies do not change with time (eg: hydrogen atom) we have a time-independent wave. The wave function is:

$$\Psi = \mathrm{A}e^{2\pi i \frac{x}{\lambda}} = \mathrm{A} \sin 2\pi \frac{x}{\lambda}$$

From this it follows that

$$\frac{d^2\Psi}{dx^2} = -\frac{4\pi^2}{\lambda^2} \mathrm{A} \sin 2\pi \frac{x}{\lambda} = -\frac{4\pi^2}{\lambda^2} \Psi$$

Total energy of hydrogen-like system is given by: $E =$ kinetic energy + potential energy between the electron and the proton. Since the relation between momentum and wave length is given by the de Broglie equation:

$$mv = \frac{h}{\lambda} \left(\text{(Recall from Chapter 1 that } \lambda = \frac{h}{p} = \frac{h}{mv} \right)$$

it follows that the kinetic and potential energies are:

$$\text{kinetic energy} = \mathrm{T} = \tfrac{1}{2}mv^2 = \frac{(mv)^2}{2m} = \frac{h^2}{2m\lambda^2}$$

$$\text{potential energy} = V = -\frac{\mathrm{Z}_1\mathrm{Z}_2e^2}{r} = -\frac{e^2}{r} (Z_1 = Z_2 = 1 \text{ for hydrogen}$$

and $r =$ electron-nucleus separation).

Then $\dfrac{d^2\Psi}{dx^2} = -\dfrac{8\pi^2 m}{h^2}\,\mathrm{T}\Psi$ so that $\mathrm{T}\Psi = -\dfrac{h^2}{8\pi^2 m}\dfrac{d^2\Psi}{dx^2}$

If the wave equation is now generalised to three dimensions (x, y, z coordinate axes) we obtain

$$-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Psi = \mathrm{T}\Psi = (E-V)\Psi$$

$$\text{or}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Psi + \frac{8\pi^2 m}{h^2}\left(E+\frac{e^2}{r}\right)\Psi = 0 \qquad \ldots (2)$$

This is Schrödinger equation which describes accurately atomic systems. This equation is also expressed as:

$$\mathscr{H}\Psi = \left[-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)-\frac{e^2}{r}\right]\Psi = E\Psi$$

The above equation means that we have to take the second partial derivative of a function Ψ, add them together, multiply by $-h^2/8\pi^2 m$, and if we now add to this $(-e^2/r)\,\Psi$ we shall have something equal to $E\,\Psi$. $\mathscr{H}$ is called the Hamiltonian operator which is called upon to perform the above instructions on Ψ. When we have found a function Ψ which allows us to do all the above operations giving an energy value corresponding to E, Ψ is said to be a solution of the Schrödinger equation and is called a wave function.

Since we take derivatives of Ψ with respect to the coordinate axes x, y, z of the electron it follows that Ψ must be a function of these coordinates. Taking the nucleus as the origin of a Cartesian coordinate frame Ψ must have a particular value for a particular set of values of x, y and z. There must be a definite probability of finding the electron at any point around the nucleus. Ψ can have both real and imaginary values but probability can have only real values. Since probability is given by the square of the amplititude of the wave function and since this can only be real we must multiply Ψ by its complex conjugate Ψ^* so that the product becomes real. Thus the probability of finding the electron within the small volume element ($d\tau$) about the point (x, y, z) is given by :

probability $= P = \Psi^*(x, y, z)\,\Psi(x, y, z)\,d\tau$

Probability of finding the electron at any point may be large, small, even zero but not imaginary. If Ψ is real then $P = \Psi^2$. Some important conclusions can now be drawn in respect of Ψ:

1. Since there must be one and only one value of the probability for a particular set of (x, y, z) values, Ψ must be single valued for a given set of (x, y, z).

2. The wave function can have only finite values. It cannot have 'infinity' as a value.

3. Taking all conceivable probability values in space around the nucleus and noting that we are dealing with the probability of one electron it follows that the total probability must be unity:

$$\int_{-a}^{+a}\int_{-a}^{+a}\int_{-a}^{+a}\Psi(x, y, z)\,\Psi^*(x, y, z)\,dx\,dy\,dz = \int \Psi\Psi^* d\tau = 1$$

where $d\tau$ is a small volume element over which the wave function has the value Ψ. When a wave function satisfies this condition it is termed a *normalised wave function.*

In order to solve the Schrödinger equation we have to express equation (2) in terms of spherical polar coordinates r, θ, ϕ. The relationship between the Cartesian and spherical coordinates is given by a study of Fig. 1.1 :

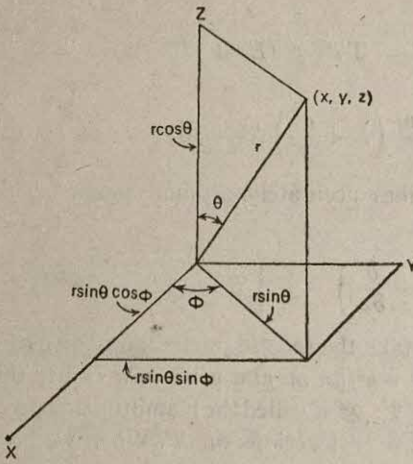

Fig. I.1. The spherical coordinate system and its relation to the Cartesian coordinate system

$$x = r \sin\theta \cos\phi$$

$$y = r \sin\theta \sin\phi$$

$$z = r \cos\theta$$

$$r = \sqrt{x^2 + y^2 + z^2}$$

Utilisation of these values of x, y, z and substitution of the operator

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

into the corresponding polar form enable us to write equation (2) in the form:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \Psi}{\partial r}\right) + \frac{1}{r^2 \sin^2\theta}\,\frac{\partial^2 \Psi}{\partial \phi^2} + \frac{1}{r^2 \sin\theta}\,\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial \Psi}{\partial \theta}\right) + \frac{8\pi^2 m}{h^2}\left(E + \frac{e^2}{r}\right)\Psi = 0 \quad \ldots (3)$$

This equation contains three variables r, θ and ϕ, and can be written as the product of three simpler functions: $R(r)$ dependent only on r, Θ (θ) dependent only on θ, and $\Phi(\phi)$ dependent only ϕ. Thus:

$$\Psi(r, \theta, \phi) = R(r)\Phi(\theta)\,\Phi(\phi) \quad \ldots (4)$$

If we substitute this expression in equation (3) and multiply by $r \sin^2\theta/\Psi$, that is by $r^2 \sin^2\theta/R.\Theta.\Phi$. we have:

$$\frac{\sin^2\theta}{R}\,\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{1}{\Phi}\cdot\frac{d^2\Phi}{d\phi^2} + \frac{\sin\theta}{\Theta}\cdot\frac{d}{d\theta}\left(\sin\theta.\frac{d\Theta}{d\theta}\right) + r^2\sin^2\theta.\frac{8\pi^2 m}{h^2}\left(E + \frac{e^2}{r}.\right) = 0 \quad \ldots (5)$$

Rearrangement gives:

$$\frac{\sin^2\theta}{R}\,\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{\sin\theta}{\Theta}\cdot\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + r^2\sin^2\theta.\frac{8\pi^2 m}{h^2}\left(E + \frac{e^2}{r}\right) = -\frac{1}{\Phi}\cdot\frac{d^2\Phi}{d\phi^2} \quad \ldots (6)$$

Since the left hand side does not contain any ϕ, and whereas the right hand side is a function only of the independent variable ϕ, the right hand side may be put equal to a constant $\overline{m}^2$. We then get,

$$\frac{1}{\Phi}\cdot\frac{d^2\Phi}{d^2\phi} = -\bar{m}^2;\ \frac{d^2\Phi}{d\phi} = -\bar{m}^2\Phi \qquad \ldots(7)$$

Substituting the above value of $\bar{m}^2$ in equation (6) and dividing by $\sin^2\theta$ we get:

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{pR}{dr}\right) - \frac{\bar{m}^2}{\sin^2\theta} + \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\,\frac{d\Theta}{d\theta}\right) + \frac{8\pi^2 mr^2}{h^2}\left(E + \frac{e^2}{r}\right) = 0 \qquad \ldots(8)$$

Rearranging we get an equation in which θ appears only on the right hand side and r on the left hand side:

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{8\pi^2 mr^2}{h^2}\left(E + \frac{e^2}{r}\right) = \frac{\bar{m}^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\,\frac{d\Theta}{d\theta}\right) \qquad \ldots(9)$$

Each part can be equated to a constant β. We now multiply the r terms by $\frac{R}{r^2}$ and θ terms by Θ, so that we get:

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - \frac{\bar{m}^2\,\Theta}{\sin^2\theta} + \beta\Theta = 0 \qquad \ldots(10)$$

$$\text{and } \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{\beta R}{r^2} + \frac{8\pi^2 m}{h^2}\left(E + \frac{e^2}{r}\right)R = 0 \qquad \ldots(11)$$

We now have a Θ equation (10), an R equation (11) and a Φ equation (7). The complete wave function for the hydrogen electron will be decided by the physically appropriate and acceptable solutions of the three equations.

The solution of the Φ equation is:

$$\Phi(\phi) = \text{constant.}\exp(i\bar{m}\phi) \qquad \ldots(12).$$

The angle ϕ may vary from 0 to 2π so that $\Phi(\phi)$ function has identical values at ϕ and $\phi + 2\pi$. Remembering that Ψ has to be single valued $\bar{m}$ must be an integer. Thus equation (12) will have solutions for $\bar{m} = 0, \pm 1, \pm 2$ etc. Thus $\bar{m}$ really gives the permissible values of the magnetic quantum numbers m_l. The value of the constant can be had by normalisation, that is, by integrating the probability between 0 to 2π and putting equal to 1:

$$\int_0^{2\pi} \Phi_{\bar{m}}(\phi)\,\Phi^*_{\bar{m}}(\phi)d\phi = 1 \text{ where } \Phi^*_{\bar{m}} = A\exp(-i\bar{m}\phi)$$

$$\text{Then}\quad A^2\int_0^{2\pi} \exp(i\bar{m}\phi)\exp(-i\bar{m}\phi)\,d\phi = A^2.2\pi = 1$$

$$\text{whence } A = \frac{1}{\sqrt{2\pi}}$$

Acceptable solutions of the Φ equation are found if β is equal to $l(l+1)$ where l can assume positive integral values including 0 and that m_l is $\leqslant l$. It therefore means that m_l values can vary from $+l$ to $-l$ in integral steps for any given l. This l is the orbital angular momentum quantum number. The R equation will yield solutions by invoking still another quantum number, n, such that

$$l = (n-1), (n-2) \ldots 0$$

This n is the principal quantum number.

Complete wave function for the hydrogen electron can be expressed as:

$$\Psi_{n,l,m_l} = R_{n,l}(r).\,\Theta_{l,m_l}.\,\Phi_{m_l}(\phi)$$

Such a wave function provides the minimum value of the energy of the electron and hence describes the electron best. Note that the $R_{n.l}(r)$ is the radial part of the wave function and is independent of the angles θ and ϕ. $\Theta_{l,m_l},.\ \Phi_{m_l}(\phi)$ is the angular part of the wave function. The high and low probability regions for any electron are associated with high and low values of $/\Psi n, l, m_l/^2$. Hence Ψ serving as a guide to the probability values can be termed an orbital to retain an analogy for the orbit of the old quantum theory.

The probability of finding an electron in a concentric spherical shell of radius r and thickness $\triangle r$ is given by $4\pi^2 r^2 \Psi^2{}_r \triangle r$($\Psi r$ = radial part of the wave function = $\Psi_{n,l}(r) = R_{n.l}(r)$, where $4\pi r^2\Psi^2{}_r$ is the radial probability distribution function. Fig. 1.17 (Chapter 1) gives the plots of $4\pi r^2\Psi^2{}_r$ vs. r for several orbitals. Angular part of the wave functions describes the angular dependence of Ψ in different directions around the nucleus. Below we discuss how the shapes of orbitals follow from the wave functions of the electrons.

I. '*s*' *Orbitals*

Quantum Numbers			Orbital symbol	Wave Function	
n	l	m_l		Radial Part	Angular Part
1	0	0	1*s*	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$	$\frac{1}{2\sqrt{\pi}}$
2	0	0	2*s*	$2^{-3/2}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$	$\frac{1}{2\sqrt{\pi}}$
3	0	0	3*s*	$\frac{2}{81}\cdot\frac{1}{\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left(27-\frac{18Zr}{a_0}+\frac{2Z^2r^2}{a_0{}^2}\right)e^{-Zr/3a_0}$	$\frac{1}{2\sqrt{\pi}}$

[$Z = 1$ for hydrogen; a_0 = Bohr radius = 0.529A]

The following points are to be noted:

1. None of the Ψ_{1s}, Ψ_{2s} or Ψ_{3s} contains any term containing θ or ϕ. So s wave functions have no angular dependence. These orbitals will have, for a particular r, the same probability all around the nucleus. They are spherically symmetrical (Fig. 1.18).

2. Ψ_{1s}, Ψ_{2s}, Ψ_{3s} have definite high values near the nucleus but the probability of finding the electron in a spherical shell close to the nucleus will be zero since

that involves the radius (*i.e.* $4\pi^2 r \Psi r^2$). Hence in Fig. 1.17 the plot of $4\pi^2 r^2 \Psi r^2$ vs. r is zero at the nucleus.

3. Ψ_{1s} has a maximum at $r = a_0 = 0.529$A. For Ψ_{2s} the value of Ψ increases (at $r/a_0 = 1$, at $r = 0.529$A), then decreases and becomes zero at $Zr/a_0 = r/a_0 \doteq 2$ (*i.e.* at $r = 2a_0 \simeq 1$A). The wave function then increases again to a maximum at ~ 2.6A and then decreases. Similarly Ψ_{3s} becomes zero at ~ $r = 2a_0$ and at ~ $r = 7a_0$. It goes to maximum at 0.529A, at ~ 2.6A and at ~6.9A. Thus Ψ_{2s} passes through one node and Ψ_{3s} through two nodes. Nodes are surfaces at which Ψ and consequently Ψ^2 go to zero. For Ψ_{ns} orbitals the number of these nodes is always $n-1$. These nodes are spherical surfaces.

4. The radial distribution function, that is, the probability density has its largest value beyond the last node.

5. Ψ_{2s} orbital has two concentric spherical regions of maximum probability, the inner one being much the smaller. Ψ_{3s} has three such concentric regions.

6. Ψ_{1s} has a + sign but for all other '*s*' orbitals the concentric shells have alternate + and − signs, the innermost region being + . The alternate + and − signs of the antinodes follow from details of the analytical expression of the radial part of the total wave function.

The conclusions embodied under 3 above follow naturally when the wave functions are analytically investigated for the existence of maximum and minimum values at discrete values of r. The necessary condition for this is that the first derivative of the wave function (or rather the square of it) should be zero at the specific values of r.

II. 'p' Orbitals: The three $2p$ orbitals have the following wave functions:

Quantum Numbers			Orbital symbol	Wave Function	
n	l	m_l		Radial Part	Angular Part
2	1	0	$2p_z$	$\frac{1}{2}\cdot\frac{1}{\sqrt{6}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right)e^{\frac{-Zr}{2a_0}}$	$\frac{1}{2}\cdot\sqrt{3}\cdot\frac{1}{\sqrt{\pi}}\cos\theta$
2	1	1	$2p_x$	,,	$\frac{1}{2}\cdot\sqrt{3}\cdot\frac{1}{\sqrt{\pi}}\sin\theta\cdot\cos\phi$
2	1	−1	$2p_y$	,,	$\frac{1}{2}\cdot\sqrt{3}\cdot\frac{1}{\sqrt{\pi}}\sin\theta\sin\phi$

The above wave functions become more meaningful and more amenable to discussion when written in the following froms:

$$\Psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{5/2} e^{-Zr/2a_0}\, r\cos\theta$$

$$\Psi_{2p_x} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{5/2} e^{-Zr/2a_0}\, r\sin\theta\cos\phi$$

$$\Psi_{2p_y} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{5/2} e^{-Zr/2a_0}\, r\sin\theta\sin\phi$$

The following points emerge:

1. The wave functions are dependent on θ and ϕ and hence cannot be spherically symmetrical.

2. At $r = 0$, the Ψ_{2px}, Ψ_{2py} and Ψ_{2pz} become zero.

3. The wave functions have their maximum values along the respective coordinate axes. Thus Ψ_{2pz} attains maximum when $\cos\theta = 1$, that is, when $\theta = 0$. At $\theta = 0$, the Ψ_{2px} and Ψ_{2py} become zero. When $\theta = 90°$ and $\phi = 90°$ then $\sin\theta \sin\phi$ is equal to 1 so that the wave function becomes maximum along y axis, and, therefore, it must be the $2p_y$ orbital. Similarly $\sin\theta\cos\phi = 1$ when θ is 90° and ϕ is 0°. We then have the $2p_x$ orbital, which has its maximum along the x axis.

4. On either side of the nucleus along the x, y or z axis the Ψ_{2p} values have opposite signs. This is easily understood from the limits of variation of θ (from 0 to π) and of ϕ (from 0 to 2π). Taking Ψ_{2px}, for instance, the $\sin\theta$ component in it always contributes positively but the $\cos\phi$ may be positive or negative in one complete cycle of ϕ values. Similarly the nature of Ψ_{2py} can also be understood. The Ψ_{2pz} orbital however assumes positive and negative values for $\theta = 0$ to $\pi/2$, and $\pi/2$ to π respectively.

The three orbitals are concentrated along the three Cartesian axes and each, while at its maximum value, reduces to

$$\Psi_{2p}\,(\text{max}) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{5/2} e^{-Zr/2a_0}\, r$$

6. The Ψ functions are such that they have no nodal surfaces. Check from Fig 1.17 that the $2p$ radial distribution function does not touch the abscissa.

7. The three $3p$ wave functions have the following forms:

$$\Psi_{3pz} = \left[\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{5/2}\left(6r - \frac{Zr^2}{a_0}\right)e^{-Zr/3a_0}\right]\cos\theta$$

$$\Psi_{3px} = \left[\qquad\qquad \text{,,} \qquad\qquad\right]\sin\theta\cos\phi$$

$$\Psi_{3py} = \left[\qquad\qquad \text{,,} \qquad\qquad\right]\sin\theta\sin\phi$$

At $6r = \dfrac{Zr^2}{a_0} = \dfrac{r^2}{a_0}$ (for H), that is at $r = 6a_0$ the wave functions reduce to zero and then assume negative sign. Therefore these orbitals will have a nodal surface at $r = 6a_0$ and will be made of two concentric dumbbells. Check from Fig 1.17 that the $3p$ radial probability distribution function becomes zero just beyond 3A.

III. *d Orbitals*. The five $3d$ orbitals can be expressed as:

$$3d_{xy} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{7/2} r^2 e^{-Zr/3a_0} \sin^2\theta \sin 2\phi$$

$$3d_{xz} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{7/2} r^2 e^{-Zr/3a_0} \sin\theta\cos\theta\cos\phi$$

$$3d_{yz} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{7/2} r^2 e^{-Zr/3a_0} \sin\theta\cos\theta\sin\phi$$

$$3d_{x^2-y^2} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{7/2} r^2\, e^{-Zr/3a_0} \sin^2\theta \cos 2\phi$$

$$3d_{z^2} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{7/2} r^2\, e^{-Zr/3a_0} (3\cos^2\theta - 1)$$

The following points emerge from a scrutiny of the above wave functions:

1. The $3d_{xy}$ orbital carries $\sin^2\theta \sin 2\phi$. Such a wave function reduces to zero along z axis (since $\theta = 0$), along x axis (since $\theta = 90°$ but $\phi = 0$) and along the y axis (since $\theta = 90°$ and $\phi = 90°$). When θ is 90° and ϕ is 45° the wave function becomes maximum in the xy plane at 90° to the z axis but at 45° from either the x or the y axis. Since the xy plane has four quadrants the orbital will have four lobes (Fig. 1.20), one in each of the four quadrants. Similar situation prevails for the other two orbitals: $3d_{xz}$ orbital having four lobes in the xz plane in between the x/z axes, and the $3d_{yz}$ orbital having its four lobes between the y and z axes. The lobes will carry alternate + and −signs.

2. The $3d_{x^2-y^2}$ orbital reduces to zero along the z axis (since $\theta = 0$ or 180°). When θ is 90° and ϕ is 0°, $\sin^2\theta \cos 2\phi$ attains maximum value, and the orbital is concentrated along x axis. Similarly when θ is 90° and ϕ is 90°, Ψ becomes maximum again, and the orbital is concentrated along the y-axis with a '−' sign. The $3d_{x^2-y^2}$ orbital is thus composed of four lobes along x and y axes on either side of the nucleus with alternate + and −signs (Fig. 1.20).

3. The $3d_{z^2}$ orbital attains maximum when θ is 0°. When θ is 90° (that is at right angles to the z-axis: along x/y axes) $\Psi 3d_{z^2}$ has negative values. Thus the orbital is concentrated along the z-axis with + sign and has a ring all around the nucleus in the xy plane with a−sign.

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Appendix II

Molecular Orbital Theory

Molecular orbital theory treats the electrons of polyatomic molecules as belonging to the molecule as a whole—instead of belonging to the respective atoms. Molecular orbitals are thus polycentric. Molecular orbitals are orbitals where molecular electrons reside.

Just as atomic orbitals have certain characteristics so also the molecular orbitals: (1) Thus molecular orbitals have a certain wave function Ψ. If Ψ is normalised we have $\Psi^2\partial\tau = 1$. (2) These wave functions have a definite energy value. (3) Energy and spatial distribution of each M.O. will be decided by a set of quantum numbers. (4) Each molecular electron has a spin $= \pm\frac{1}{2}$ like that of atomic electrons. (5) Like atomic orbitals M.O.'s also can accommodate a maximum of two electrons i.e. they too obey Pauli Exclusion Principle.

The quantum mechanical basis of the M.O. theory will be developed for the simplest case of combining two atomic orbitals to generate M.O.'s. For effective generation of M.O.'s the following three conditions are to be met: (1) the combining A.O.'s should be close in their energy values; (2) they should overlap well and (3) their overlap should be permitted by symmetry.

The method of *linear combination of atomic orbitals* (*LCAO*) *is used.* A linear combination of two wave functions is obtained by multiplying each by some constant and then adding. If we subject an '*s*' orbital to the pull of a positive nucleus i.e. a positive field along the *x* axis then some of the electron cloud will be flattened out along the *x* axis, resembling somewhat a p_x orbital. Thus the 'deshaped' orbital will pertake characteristics of both the *s* orbital and a *p* orbital. If our combining orbitals have their wave functions as Ψ_A and Ψ_B then the M.O. wave function may be represented as:

$$\Psi = C_A \Psi_A + C_B \Psi_B \qquad \ldots (1)$$

where C_A and C_B are such constants that will lead to a minimum energy expression for the wave function.

We recall that the Schrödinger equation may be written as :

$$\nabla^2 \Psi + \frac{8\pi^2 m}{h^2} (E-V) \Psi = 0 \qquad \ldots (12)$$

$$\left(\text{where} \qquad \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

This can be rearranged to the following form:

$$\left(-\frac{h^2}{8\pi^2 m} \nabla^2 + V\right) \Psi = E\Psi \qquad \ldots (3)$$

$$\text{i.e.} \qquad \mathcal{H} \Psi = E\Psi \qquad \ldots (4)$$

where $\mathcal{H}$ is the Hamiltonian operator.

We can further write the equation (4) as:

$$\Psi\mathcal{H}\Psi = \Psi E \Psi \text{ where } \int \Psi\mathcal{H}\Psi\,\partial\tau = \int \Psi E \Psi \partial\tau = E \int \Psi^2 \partial\tau$$

so that the energy of the wave function is given by:

$$E = \frac{\int \Psi \mathcal{H} \Psi \partial\tau}{\int \Psi^2 \partial\tau} \qquad \ldots (5)$$

Now putting $\Psi = C_A \Psi_A + C_B \Psi_B$ we shall explore the conditions that minimise the energy. So long as the energy is not minimised we shall use $\mathscr{E}$ as the energy function:

$$\mathscr{E} = \frac{\int (C_A \Psi_A + C_B \Psi_B) \mathcal{H} (C_A \Psi_A + C_B \Psi_B) \partial\tau}{\int (C_A \Psi_A + C_B \Psi_B)^2 \partial\tau} \qquad \ldots (6)$$

$$= \frac{C^2_A \int \Psi_A \mathcal{H} \Psi_A \partial\tau + C_A C_B \int \Psi_A \mathcal{H} \Psi_B \partial\tau + C_A C_B \int \Psi_B \mathcal{H} \Psi \partial\tau + C^2_B \int \Psi_B \mathcal{H}_B \partial\tau}{C^2_A \int \Psi_A^2 \partial\tau + 2C_A C_B \int \Psi_A \Psi_B \partial\tau + C_B^2 \int \Psi_B^2 \partial\tau} \qquad \ldots (7)$$

Now we put simplifying relation $\int \Psi_A \mathscr{H} \Psi_B \partial\tau = \int \Psi_B \mathscr{H} \Psi_A \partial\tau$

$$\mathscr{E} = \frac{C^2_A \int \Psi_A \mathscr{H} \Psi_A \partial\tau + 2C_A C_B \int \Psi_A \mathscr{H} \Psi_B \partial\tau + C^2_B \int \Psi_A \mathscr{H} \Psi_B \partial\tau}{C_A^2 \int \Psi_A^2 \partial\tau + 2C_A C_B \int \Psi_A \Psi_B \partial\tau + C_B^2 \int \Psi_B^2 \partial\tau} \quad \ldots (8)$$

It can also be shown without the simplifying assumption that $\int \Psi_A \mathscr{H} \Psi_B \partial\tau = \int \Psi_B \mathscr{H} \Psi_A \partial\tau$. Recall that the Hamiltonian operator $\mathscr{H}$ carries a differential ∇^2 term which has components like $\partial^2/\partial x^2$ etc. If we carry on the integration procedures we have:

$$\int \Psi_A \mathscr{H} \Psi_B \partial\tau = \int \Psi_A \frac{\partial^2 \Psi_B}{\partial x^2} \partial\tau = \left[\Psi_A \frac{\partial \Psi_B}{\partial x}\right] - \int \frac{\partial \Psi_A}{\partial x} \frac{\partial \Psi_B}{\partial x} \partial\tau$$

$$= \left[\Psi_A \frac{\partial \Psi_B}{\partial x}\right] - \left[\Psi_B \frac{\partial \Psi_A}{\partial x}\right] + \int \Psi_B \frac{\partial^2 \Psi_A}{\partial x^2} \partial\tau$$

Our implicit assumption is that both Ψ_A and Ψ_B functions are acceptable wave functions. Then both Ψ_A and Ψ_B will vanish at infinity. Then we can write:

$$\int \Psi_A \mathscr{H} \Psi_B \partial\tau = \int \Psi_A \frac{\partial^2 \Psi_B}{\partial x^2} \partial\tau = \int \Psi_B \frac{\partial^2 \Psi_A}{\partial x^2} \partial\tau = \int \Psi_B \mathscr{H} \Psi_A \partial\tau$$

Also note that the potential energy term, V, contained within $\mathfrak{H}$ remains the same because it stands for the sumtotal effect of electron–electron, proton–proton and electron–proton interactions.

We now introduce the following simplifying notations:

$$\int \Psi_A \mathfrak{H} \Psi_A \partial\tau = H_{AA} \;;\; \int \Psi_A \mathfrak{H} \Psi_B \partial\tau = H_{AB}$$

$$\int \Psi_B \mathfrak{H} \Psi_B \partial\tau = H_{BB} \;;\; \int \Psi^2_A \partial\tau = S_{AA}$$

$$\int \Psi_A \Psi_B \partial\tau = S_{AB} \;;\; \int \Psi^2_B \partial\tau = S_{BB}$$

$$\mathscr{E} = \frac{C^2_A H_{AA} + 2C_A C_B H_{AB} + C^2_B H_{BB}}{C^2_A S_{AA} + 2C_A C_B S_{AB} + C^2_B S_{BB}} \quad \ldots (9)$$

This relation can be rearranged to give:

$$C^2_A(H_{AA} - \mathscr{E} S_{AA}) + 2C_A C_B(H_{AB} - \mathscr{E} S_{AB}) + C^2_B(H_{BB} - \mathscr{E} S_{BB}) = 0 \quad \ldots (10)$$

When we arrive at that minimum energy ($\mathscr{E} = E$) for the M. O. wave function then $\frac{\partial \mathscr{E}}{\partial C_A} = 0$ and $\frac{\partial \mathscr{E}}{\partial C_B} = 0$. We now differentiate the above expression with respect to C_A and put the condition $\frac{\partial \mathscr{E}}{\partial C_A} = 0$

$$2C_A(H_{AA} - \mathscr{E} S_{AA}) + C^2_A\left(0 - \frac{\partial \mathscr{E}}{\partial C_A} S_{AA}\right) + 2C_B(H_{AB} - \mathscr{E} S_{AB}) + 2C_A C_B\Big(0 -$$

$$\frac{\partial \mathscr{E}}{\partial C_A} S_{AB}\Big) + 0(H_{BB} - \mathscr{E} S_{BB}) + C^2_B\left(0 - \frac{\partial \mathscr{E}}{\partial C_B} S_{BA}\right) = 0 \quad \ldots (11)$$

Therefore $C_A(H_{AA} - ES_{AA}) + C_B(H_{AB} - ES_{AB}) = 0$ $\quad \ldots (12)$

Differentiating with respect to C_B and putting the condition $\frac{\partial \mathscr{E}}{\partial C_B} = 0$ gives the following relation:

$$C_A(H_{AB}-ES_{AB}) + C_B(H_{BB}-ES_{BB}) = 0 \qquad \ldots (13)$$

Dividing (12) and (13) by C_A and putting $\lambda = \frac{C_B}{C_A}$ we have:

$$(H_{AA} - ES_{AA}) + \lambda(H_{AB} - ES_{AB}) = 0 \qquad \ldots (14)$$

$$(H_{AB} - ES_{AB}) + \lambda(H_{BB} - ES_{BB}) = 0 \qquad \ldots (15)$$

Now let us reexamine H_{AA}, H_{BB}, H_{AB}, S_{AA}, S_{AB}, and S_{BB}.

$$H_{AA} = \int \Psi_A \mathscr{H} \Psi_A \partial\tau = \int \Psi_A E_A \Psi_A \partial\tau = E_A \int \Psi^2{}_A \partial\tau = E_A$$

$$H_{BB} = \int \Psi_B \mathscr{H} \Psi_B \partial\tau = \int \Psi_B E_B \Psi_B \partial\tau = E_B \int \Psi^2{}_B \partial\tau = E_B$$

$$\mathscr{H}_{AB} = \int \Psi_A \mathscr{H} \Psi_B \partial\tau = \beta \,;\, S_{AA} = \int \Psi^2{}_A \partial\tau = 1$$

$$S_{BB} = \int \Psi^2{}_B \partial\tau = 1 \,;\, S_{AB} = \int \Psi_A \Psi_B \partial\tau = S$$

Then equations (14) and (15) take the form:

$$(E_A - E) + \lambda(\beta - ES) = 0 \qquad \ldots (16)$$

$$(\beta - ES) + \lambda(E_B - E) = 0 \qquad \ldots (17)$$

So that $$(E_A-E)(E_B-E) = (\beta-ES)^2 \qquad \ldots (18)$$

Such a relation will provide two solutions for the energy E of the molecular orbitals formed by way of linear combination of the two atomic orbitals Ψ_A and Ψ_B. To arrive at the solutions we assume relative values of E_A and E_B. Let $E_A \leqslant E_B$. Since the larger the energy of the orbital the larger is the size of the orbital we have $\Psi_A \leqslant \Psi_B$. If the orbitals are of similar size their overlap integral may approach a maximum of 1. It should be noted that S will be zero when the two orbitals do not overlap at all. It should also be appreciated that when the two orbitals vary in their sizes greatly—as in our case—their overlap integral S will also be small. It can be shown that if S is small so also is β. This is done for H_2^+ below.

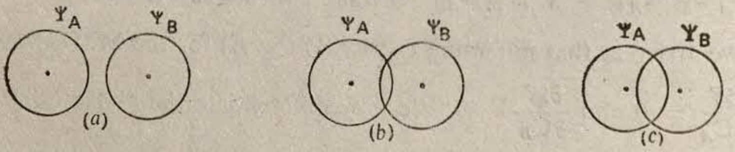

Fig. II. 1 Overlap Integral: (a) no overlap; $S = O$; (b) small overlap; $S \ll 1$ and (c) large overlap; $S \simeq 1$

In H_2^+ there is but a single electron moving in the presence of two nuclei A and B. The wave equation takes the form:

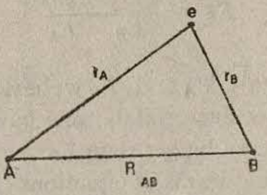

Fig. II.2

$$\nabla^2 \Psi + \frac{8\pi^2 m}{h^2}\left(E + \frac{e^2}{r_A} + \frac{e^2}{r_B} - \frac{e^2}{R_{AB}}\right)\Psi = 0 \qquad \ldots (19)$$

$$\left(\text{Note } V = -\frac{e^2}{r_A} - \frac{e^2}{r_B} + \frac{e^2}{R_{AB}}\right)$$

Ignoring the e^2/R_{AB} term the Hamiltonian is:

$$\mathscr{H} = -\frac{h^2}{8\pi^2 m}\nabla^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B}$$

$$\text{Then } \mathscr{H}\,\Psi = \left(-\frac{h^2}{8\pi^2 m}\nabla^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B}\right)\Psi$$

If we neglect the second nucleus B then we have:

$$\left(-\frac{h^2}{8\pi^2 m}\nabla^2 - \frac{e^2}{r_A}\right)\Psi_A = E_A\Psi_A$$

$$\begin{aligned}
\beta &= \int \Psi_A \mathscr{H}\, \Psi_B \partial\tau = \int \Psi_B \mathscr{H}\, \Psi_A \partial\tau \\
&= \int \Psi_B\left(-\frac{h^2}{8\pi^2 m}\nabla^2 - \frac{e^2}{r_A} - \frac{e^2}{r_B}\right)\Psi_A \partial\tau \\
&= \int \Psi_B\left(E_A - \frac{e^2}{r_B}\right)\Psi_A \partial\tau \\
&= E_A \int \Psi_B \Psi_A \partial\tau - \int \frac{e^2}{r_B}\Psi_A \Psi_B \partial\tau \\
&= E_A S - \int \frac{e^2}{r_B}\Psi_A \Psi_B \partial\tau \qquad \ldots (20)
\end{aligned}$$

Thus we see that if S is small β will also be small. So $(\beta - ES)^2$ is small quantity. The necessary condition for this is that either $(E_A - E)$ or $(E_B - E)$ is small (cf : Eq. 18). Let us take the case that $(E_A - E)$ is small, which means that $E_A \simeq E$. In equation (18) we can put $E = E_A$ such that the relation does not vanish identically. Thus:

$$(E_A - E)(E_B - E_A) = (\beta - E_A S)^2 \qquad \ldots (21)$$

$$\text{whence } E_A - E = \frac{(\beta - E_A S)^2}{E_B - E_A}\ ;\ E = E_A - \frac{(\beta - E_A S)^2}{E_B - E_A} \qquad \ldots (22)$$

If we assume $E_B - E$ is small so that $E \simeq E_B$, then we have:

$$E = E_B + \frac{(\beta - E_B S)^2}{E_B - E_A} \qquad \ldots (23)$$

Thus starting with two orbitals Ψ_A and Ψ_B we have two energies of the M.O.'s *i.e.* we have generated two molecular orbitals: one having an energy lower than E_A and the other having an energy higher than E_B. Since $E_B - E_A$ is large according to our assumptions the second terms in equations (22) and (23) are very small so that the solutions of the two M.O.'s will become almost the same energies as those of the starting atomic orbitals.

It is also evident that if the Ψ_A and Ψ_B do not overlap at all then the overlap integral S as well as the resonace integral β are zero (cf: equation 20). This means the energies of the M.O.'s reduce to E_A and E_B (cf: equations 22 and 23). *Thus overlap of the combining A.O.'s is essential for effective formation of the M.O.'s.*

We can further investigate the conditions when S and β reduce to zero. Both S and β will reduce to zero when the two combining A.O.'s overlap in such a way that there are two regions of equal magnitude but opposite sign. Thus the overlap of one s orbital of atom A with that of a p_z orbital of a second atom B (Fig. II.3) gives an overlap integral for the upper half which is exactly equal in magnitude but opposite in sign to that of the lower half. The overlap integral $\int \Psi_A \Psi_B \partial\tau$ is identically zero. Such wave functions are called *orthogonal* to each other. Therefore *for an effective formation of M.O.'s overlap of the atomic orbitals must be permitted by symmetry.* It is worthwhile to remember that (a) atomic orbitals of s, p, d, f symmetry types of one and the same atom are orthogonal and (b) that among the same orbital type of one and the same atom one orbital is orthogonal to another eg: p_x is orthogonal to p_y and p_z of the same atom.

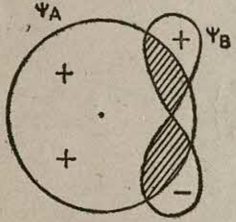

Fig. II 3. Overlap of an s orbital and a pz orbital; $S = 0$

We shall now extend our theory to the simplest possible molecule ion H_2^+. Here we have two hydrogen nuclei but only one electron. Equations (16) and (17) can be manipulated to give:

$$\lambda^2 = \frac{(E_A - E)(\beta - ES)}{(\beta - ES)(E_B - E)} \qquad \ldots (24)$$

Here the combining A.O.'s will be identical i.e. of the same hydrogen atom type. Then since $E_A = E_B$ the above relation reduces to $\lambda^2 = 1$ whence we have $\lambda = \pm 1$. So the two M.O. wave functions will be the linear combinations of the type (a) $\Psi_A + \Psi_B$ and (b) $\Psi_A - \Psi_B$.

Putting $E_A = E_B$ in equation (18) we have:

$$(E_A - E)^2 = (\beta - ES)^2 \qquad \ldots (25)$$

Then $E_A - E = \pm(\beta - ES)$ $\qquad \ldots (26)$

We now have two solutions:

$$E = \frac{E_A + \beta}{1 + S} = E_A + \frac{\beta - E_A S}{1 + S} \qquad \ldots (27)$$

$$E = \frac{E_A - \beta}{1 - S} = E_A - \frac{\beta - E_A S}{1 - S} \qquad \ldots (28)$$

Making further approximations ($S \simeq 0$) we have:

$$E = E_A + \beta \text{ and } E = E_A - \beta \qquad \ldots (29)$$

The solutions of equation (29) correspond to the M.O.'s $\Psi_A + \Psi_B$ and $\Psi_A - \Psi_B$. Since β is negative i.e. lowers energy (cf: equation 20) the $\Psi_A + \Psi_B$ forms the bonding M.O. while $\Psi_A - \Psi_B$ forms the antibonding M.O. (cf: Figs. 5.6 and 5.7 in Chapter 5).

Shapes of molecular orbitals: Taking the hydrogen atomic orbital wave functions as Ψ_A and Ψ_B, it is possible to calculate β and S for any chosen internuclear distance R. A plot of the energy of the M.O. $\Psi_A + \Psi_B$ against R shows a minimum while that of the M.O. $\Psi_A - \Psi_B$ has no minimum. This means that the M.O. $\Psi_A + \Psi_B$ is stable while the other M.O. $\Psi_A - \Psi_B$ is unstable. The M.O. $\Psi_A + \Psi_B$ has a larger value for its Ψ^2 in between the nuclei than the individual Ψ^2_A and Ψ_B^2. On the other hand the M.O. $\Psi_A - \Psi_B$ has a lower value of Ψ^2 compared to Ψ_A^2 and

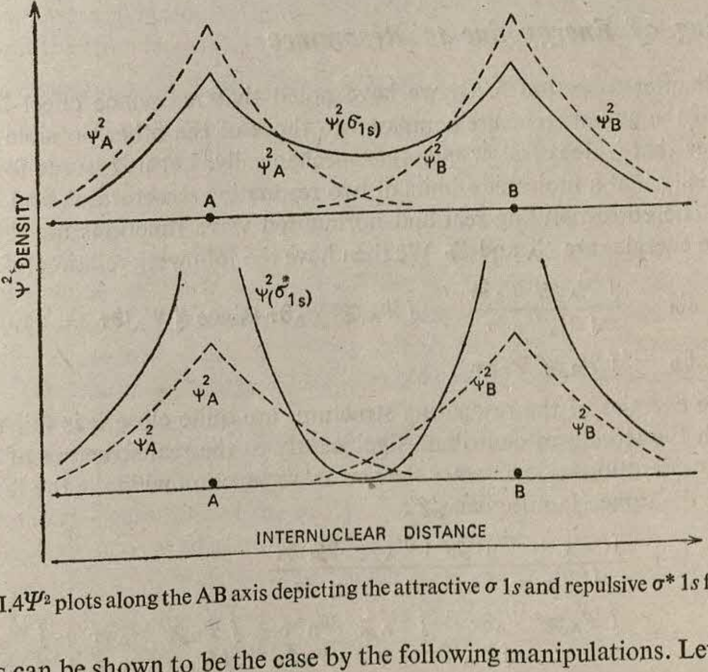

Fig. II.4 Ψ^2 plots along the AB axis depicting the attractive σ 1s and repulsive σ^* 1s for H_2^+

Ψ_B^2. This can be shown to be the case by the following manipulations. Let the two M.O. wave functions be:

$$\Psi_{bonding} = N_b(\Psi_A + \Psi_B)$$

$$\Psi_{antibonding} = N_a(\Psi_A - \Psi_B)$$

where N_b and N_a are the respective normalising constants. Assuming the M.O. wave functions are normalised we have:

$$\int \Psi^2_{bonding}\,\partial\tau = N_b^2\left[\int \Psi^2_{\mathrm{A}}\partial\tau + 2\int \Psi_{\mathrm{A}}\Psi_{\mathrm{B}}\partial\tau + \int \Psi^2_{\mathrm{B}}\partial\tau\right] = 1$$

Taking Ψ_{A} and Ψ_{B} as normalised we have:

$$N_b^2\,[1 + 2S + 1] = 1 \qquad \therefore\ N_b = \frac{1}{\sqrt{2+2S}} = \frac{1}{\sqrt{2}}\ \text{(when } S \simeq 0)$$

Then $\Psi^2_{bonding} = \frac{1}{2}\,[\Psi^2_{\mathrm{A}} + 2\,\Psi_{\mathrm{A}}\,\Psi_{\mathrm{B}} + \Psi^2_{\mathrm{B}}]$

The square of the antibonding M.O. wave function will have $-2\,\Psi_{\mathrm{A}}\,\Psi_{\mathrm{B}}\partial\tau$—thus having lesser electron density in between the two nuclei. Thus $\Psi_{\mathrm{A}} + \Psi_{\mathrm{B}}$ is an attractive M.O. while $\Psi_{\mathrm{A}} - \Psi_{\mathrm{B}}$ is a repulsive M.O. (Fig. II. 4)

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Appendix III

Lowering of Energy due to Resonance

In Chapter 5 section 5.2.1. we have noted that resonance effect lowers the energy of the actual structure compared to those of the other possible ones. We now show that it does follow quantum mechanically. Let us assume for the sake of simplicity that a molecule admits of two resonating structures A and B of close energy. The corresponding real and normalised wave functions are Ψ_{A} and Ψ_{B} while the energies are E_{A} and E_B. We then have the following relation (cf: App II):

$$E_A = \frac{\int \Psi_{\mathrm{A}}\mathscr{H}\,\Psi_{\mathrm{A}}\partial\tau}{\int \Psi_{\mathrm{A}}\,\Psi_{\mathrm{A}}\partial\tau} = \int \Psi_{\mathrm{A}}\mathscr{H}\,\Psi_{\mathrm{A}}\partial\tau\ \text{(since } \int \Psi_{\mathrm{A}}^2\partial\tau = 1)$$

$$E_B = \int \Psi_{\mathrm{B}}\mathscr{H}\,\Psi_{\mathrm{B}}\partial\tau$$

Since the energies of the resonating structures are quite close it is fair to assume that both the structures contribute significantly to the real structure of energy E. From considerations of symmetry the new wave function will take the form $\Psi_{\mathrm{A}} + \Psi_{\mathrm{B}}$ with the same Hamiltonian $\mathscr{H}$.

$$E = \frac{\int(\Psi_{\mathrm{A}} + \Psi_{\mathrm{B}})\,\mathscr{H}\,(\Psi_{\mathrm{A}} + \Psi_{\mathrm{B}})\partial\tau}{\int(\Psi_{\mathrm{A}} + \Psi_{\mathrm{B}})\,(\Psi_{\mathrm{A}} + \Psi_{\mathrm{B}})\partial\tau}$$

$$= \frac{\int \Psi_{\mathrm{A}}\mathscr{H}\,\Psi_{\mathrm{A}}\partial\tau + \int \Psi_{\mathrm{A}}\mathscr{H}\,\Psi_{\mathrm{B}}\partial\tau + \int \Psi_{\mathrm{B}}\mathscr{H}\,\Psi_{\mathrm{A}}\partial\tau + \int \Psi_{\mathrm{B}}\,\mathscr{H}\,\Psi_{\mathrm{B}}\partial\tau}{\int \Psi_{\mathrm{A}}^2\partial\tau + \int \Psi_{\mathrm{A}}\Psi_{\mathrm{B}}\partial\tau + \int \Psi_{\mathrm{B}}\,\Psi_{\mathrm{A}}\partial\tau + \int \Psi_{\mathrm{B}}^2\,\partial\tau}$$

$$= \frac{E_A + \beta + \beta + E_B}{1 + S + S + 1} = \frac{E_A + \beta}{1 + S}$$

(assuming $E_{\mathrm{A}} \simeq E_{\mathrm{B}}$)

Note that the terms $\int \Psi_A \mathscr{H} \Psi_B \partial\tau$ and $\int \Psi_B \mathscr{H} \Psi_A \partial\tau$ are the respective resonance integrals (β in App. II). We have already demonstrated that β has a negative sense i.e. it helps to lower the energy of a system due to resonance.

Appendix IV

Electronic Transition Selection Rules

An electronic transition can occur when there is a change in the dipole moment of the system from that in the ground state to that in the excited state. The larger this change the more favoured the transition is. Oscillator strength*, f, of a transition is given by:

$$f = \text{a constant. } v.\ P^2$$

where v is the frequency of the transition and P is the transition moment integral:

$$P = \int \Psi_a M \Psi_b \partial\tau$$

M is the dipole moment operator operating between the ground state and the excited state wave functions. Dipole moment has a magnitude and a direction. Thus M has the transformation properties as those of cartesian axes. Thus:

$$f = \text{a constant. } v \{(\int \Psi_a M_x \Psi_b \partial\tau)^2 + (\int \Psi_a M_y \Psi_b \partial\tau)^2 + (\int \Psi_a M_z \Psi_b \partial\tau)^2\}$$

Since M_x, M_y, M_z have the odd properties of the cartesian axes it follows that the integrands will be odd functions if both Ψ_a and Ψ_b are even or both are odd. Integral of an odd function between the limits $+\propto$ to $-\propto$ will be zero. But if Ψ_a and Ψ_b have even-odd or odd-even relation then the integrand will be an even function and the integral will have a value. In order for a transition to occur f must have a value i.e. the integrals must not vanish. So we have the important selection rule that both the wave functions must not be of the same parity. The *d-d* transitions are forbidden as are *p-p* transitions. But $p \rightarrow d$ transitions are allowed. Therefore the Laporte selection rule states: those electronic transitions are allowed where $\triangle l = \pm 1$.

This selection rule may be arrived at via symmetry properties of a complex also. Each transition moment integral is a number which will remain invariant on all symmetry operations of the group to which the complex belongs. In octahedral group the A_{1g} representation alone remains invariant on all symmetry operations. Hence the above integrands must have A_{1g}. M_x has 'ungerade' (u) parity, a p orbital also has u parity while a d-orbital has g parity. So it follows that *d-d* transition gives $g \times u \times g = u$ parity as also *p-p* transition gives $u \times u \times u = u$. But $p \rightarrow d$ transition give $u \times u \times g = g$ parity as is demanded by the A_{1g} representation.

---

* Oscillator strength is directly proportional to extinction coefficient.

Ψ_a and Ψ_b are the total wave functions of the two states between which the electronic transition occurs. These wave functions can be factorised into a space (orbital) part and a spin part. Spin has nothing to do with the dipole moment.

$$P = \int \Psi^0{}_a M \Psi^0{}_b \partial\tau \int \Psi^s{}_a \Psi^s{}_b \partial\tau$$

Spin wave functions are ill understood. However by analogy with the orthogonality rules of the orbital wave functions we have:

$$\int \Psi^s{}_a \Psi^s{}_b \partial\tau = 0 \text{ when } \Psi^s{}_a \neq \Psi^s{}_b$$

$$\int \Psi^s{}_a \Psi^s{}_b \partial\tau = 1 \text{ when } \Psi^s{}_b = \Psi^s{}_b$$

These relations immediately tell us that in order that P and hence f can be non-zero, $\Psi^s{}_a$ has to be equal to $\Psi^s{}_b$. Thus we have the second selection rule: those electronic transitions are permitted where $\triangle S = 0$

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Appendix V

Electron Spin Resonance and Evidence in Favour of Overlap of Orbitals

An electron has spin $s = \frac{1}{2}$ while its spin magnetic quantum number, m_s, may be $+\frac{1}{2}$ or $-\frac{1}{2}$. In the absence of an applied magnetic field the two m_s states are degenerate. However, on the application of a magnetic field a separation of the two m_s states takes place.

$$\bar{\mu} = \frac{-e}{mc}(m_s) \quad \text{(the negative sign stands for that of the electronic charge)}$$

$$= -\frac{e}{mc}\left(-\tfrac{1}{2}\right)\frac{h}{2\pi} = \tfrac{1}{2}.2.\frac{eh}{4\pi mc}$$

$$= \tfrac{1}{2}g\beta\,(\text{g} = 2)$$

It folows that for the $m_s = +\frac{1}{2}$ state $\bar{\mu}$ will be $-\frac{1}{2}g\beta$.

Now that the electron has two specified directions of spin, expressed by the two m_s values, the moments will be given by $(\frac{1}{2})g\beta$. and $(-\frac{1}{2})g\beta$. Recall here that a J vector has $+J$ to $-J$ number of M_J values. Each of the different M_J values represents the effective contribution along the field direction although for all the M_J values the vector is the same i.e. J. Again interaction with a magnetic field lowers the energy ($E = -\bar{\mu}H$), which is expressed by incorporation of '—' sign. It follows that the $m_s = -\frac{1}{2}$ will form the lower energy state while $m_s = +\frac{1}{2}$ will be the excited state. On feeding the electron with the energy $g\beta H$ it will make a transition from $m_s = -\frac{1}{2}$ to the $m_s = +\frac{1}{2}$ state.

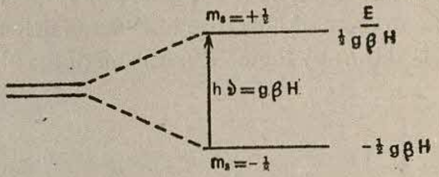
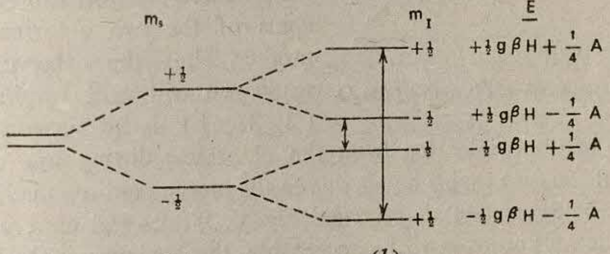


Fig. V. 1 Splitting of the m_s states of an electron in applied magnetic field.



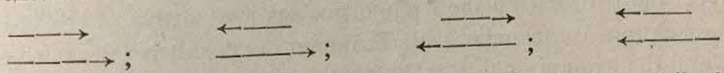
m_s
m_I
E
$+\frac{1}{2}$
$-\frac{1}{2}$
$+\frac{1}{2}$
$-\frac{1}{2}$
$-\frac{1}{2}$
$+\frac{1}{2}$
$+\frac{1}{2} g\beta H + \frac{1}{4} A$
$+\frac{1}{2} g\beta H - \frac{1}{4} A$
$-\frac{1}{2} g\beta H + \frac{1}{4} A$
$-\frac{1}{2} g\beta H - \frac{1}{4} A$

(*a*) (*b*)

Fig. V. 2. (a) The two energy states of the spinning electron in a magnetic field. (b) Nuclear spin effects on the spin of the electron.

The above situation changes radically when the unpaired electron is in the vicinity of one or more nuclei with a nuclear spin *I*. Take the simplest case of a hydrogen atom which is composed of a proton around which an electron continues to spin. The hydrogen nucleus, namely a proton, again has two nuclear spin quantum numbers. $m_I = +\frac{1}{2}$ and $m_I = -\frac{1}{2}$. It follows that for each of the two spin quantum numbers of the electron the proton also exhibits two nuclear spin quantum numbers. A total of four spin states may be possible—each one having a particular energy value. The energies of these four different states are given by: $E = g\beta m_s H + A m_s m_I$ where *A* is known as the *hyperfine coupling constant*. However, the possible transitions are guided by the selection rules:

(a) $\Delta m_s = \pm 1$; (b) $\Delta m_I = 0$. A qualitative picture of the four situations is represented as:



where the longer arrow stands for the spin direction of the electron while the smaller arrow indicates that of the nucleus. The selection rule permits only two transitions as shown in Fig. V. 2. Conceptually the selection rule shows that while the electron changes its spin direction the nuclear spin remains unaltered. In other words if the electron spin and the nuclear spin are parallel prior to the transition they will be antiparallel after the transition and vice versa:

1. $m_s = -\frac{1}{2}$; $m_I = +\frac{1}{2}$ to $m_s = +\frac{1}{2}$; $m_I = +\frac{1}{2}$
2. $m_s = -\frac{1}{2}$; $m_I = -\frac{1}{2}$ to $m_s = +\frac{1}{2}$: $m_I = -\frac{1}{2}$

Thus an electron will show two absorption peaks in its *ESR* spectrum when it is in the vicinity of a proton with nuclear spin $I = \frac{1}{2}$ i.e. the number of allowed transitions is given by $2I + 1$. In general when an unpaired electron is split by *n* equivalent nuclei of spin I_i there will be a total of $2n\ I_i + 1$ transitions. Further, if the electron is under the influence of two sets of non-equivalent nuclei, e.g. n number of spin I_i and m number of spin I_j, the total number of *ESR* transitions will be given by $(2n\ I_i + 1)\ (2m\ I_j + 1)$.

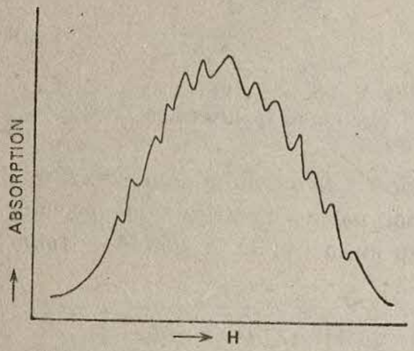


Fig. V. 3. *ESR* spectrum of $Na_2[IrCl_6]\ 6H_2O$

A remarkable case of electron delocalisation of a metal ion into ligand orbitals is shown by the *ESR* spectrum of the $Na_2[IrCl_6]\ 6H_2O$ of quadrivalent iridium (d^5; ${}^2T_{2g}$; $S = 1$) crystallised in diamagnetic host lattice of $Na_2\ [PtCl_6]\ 6H_2O$ to avoid any antiferromagnetic interaction. The expected single resonance line due to the single unpaired electron is split into a large number of bands (Fig. V. 3). Each of ${}^{35}Cl$ and ${}^{37}Cl$ has a nuclear spin $\simeq 3/2$ and ${}^{193}Ir$ has also $I = \frac{3}{2}$. If the magnetic field is applied parallel to either x, or y axis then the unpaired electron will feel the nuclear spins of the two chlorines and its own mother. Thus the otherwise single spin resonance will split up into $(2\times\frac{3}{2} + 1)$ $(2\times3 + 1) = 28$ superhyperfine lines. Some of the bands originating from the chlorine splitting are covered under the envelop of the four major bands due to the mother iridium nucleus $(2\times\frac{3}{2} + 1)$ $= 4$. In fact the experimental spectrum (Fig. V. 3) does register a large number of peaks. For such a spectrum to be acceptable, the obvious conclusion is that the unpaired electron of iridium (IV) must be moving into the orbitals of the chloride anions so as to be influenced by the nuclear spin of the chloride anions. In other words *ESR* results prove that there is an overlap between metal orbital and ligand orbitals. Along the z axis only four lines are observed due to splitting by the Ir nucleus. Obviously the two Cl^- ions are at greater distance than those along the x and y axes (cf: Jahn-Teller effect). It is interesting to note that the *ESR* spectrum of $(NH_4)_2[IrCl_6]$ crystallised in diamagnetic $(NH_4)_2\ [PtCl_6]$ shows but four lines due to hyperfine splitting by the iridium nucleus irrespective of the axis chosen for the application of magnetic field. The ammonium salt is thus parfectly cubic in nature and the iridium–chlorine distance is too long to cause any super hyperfine splitting.

The complex $[Mo(CN)_8]^{3-}$ (enriched in ${}^{13}C$; Mo^V; $4d^1$) also shows marked hyperfine splitting. Note that molybdenum (V) is coordinated to the carbon atoms of the CN^- anions. Again ${}^{12}C$ has no nuclear spin but ${}^{13}C$ has nuclear spin $I = \frac{1}{2}$.

ESR spectrum has also provided good evidence in favour of antiferromagnetism found in some oxo-vanadium (IV) and copper (II) complexes. It may be noted that in oxo-vanadium (IV) the unpaired electron ($3d^1$ system) is located in the $3d_{xy}$ orbital.* The mechanism of antiferromagnetism involves direct overlap of the $3d_{xy}$ orbitals of the two ($n = 2$) neighbouring oxo-vanadium (IV). Vanadium has a nuclear spin of $I = 7/2$ so that $2nI + 1 = 15$. Magnetically concentrated oxo-vanadium (IV) complexes often exhibit ~ 15 lines in their *ESR* spectra. On the other hand copper has $I = 3/2$. Its unpaired electron is usually in the $3d_{x^2-y^2}$ orbital and antiferromagnetism often operates through δ bond. Copper (II) complexes of such magnetically concentrated type often shows $2nI + 1 = 7$ lines in the *ESR* spectra (eg: copper (II) acetate monohydrate).

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* Crystal field splitting order: $d_{xy} < d_{xz},\ d_{yz} < d_{x^2-y^2} < d_{z^2}$

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Appendix VI

Acid-Base Titrations and Choice of Indicators

In analytical titrimetric determinations of acids and bases four distinct cases may arise, namely (a) titration of a strong acid with a strong base, (b) titration of a weak acid with a strong base, (c) titration of a weak base with a strong acid and (d) titration of a weak acid with a weak base. A knowledge of the theoretical (i.e. calculated) titration curve is essential for a proper selection of the indicator to mark the end point i.e. neutralisation point of the proposed acid-base titration.

I. Titration of a strong acid with a strong base:

The two reactants, being strong in their character, are completely dissociated in solution and moreover the salt formed is not hydrolysed. Take the case of 100 ml *N* HCl being titrated with *N* NaOH. The pH of *N* HCl is 0. When 50 ml *N* NaOH is added, the acid concentration becomes $(50 \times 1)/(100 + 50) = 3.33 \times 10^{-1}$ *N*. The pH becomes 0.48; when 90 ml *N* NaOH is added $[H^+] = (10 \times 1)/(100 + 90) = 5.27 \times 10^{-2}$; pH = 1.3; on the addition of 99.9 ml *N* NaOH the pH is 3.3. On the addition of 100.1 ml *N* NaOH the $[OH^-] = (0.1 \times 1)/(100 + 100.1) = 5.00 \times 10^{-4}$ so that pOH = 3.3. Then pH = 14−3.3 = 10.7. *Thus at the equivalance point the pH changes over the wide range* 3 to 10.5 *allowing us to use any indicator for the titration* (Table 8.7). The reader may check that similar calculation for titration of 0.1*N* HCl with 0.1*N* NaOH provides a narrower pH range, namely 4.5 to 9.5 and so on.

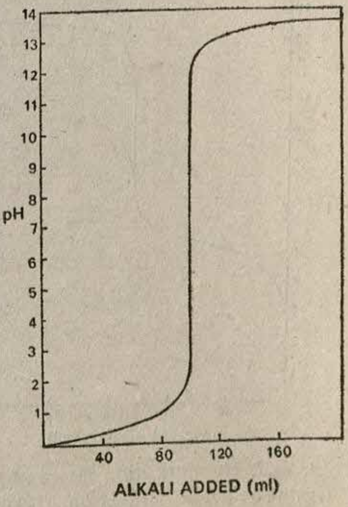


Fig. VI.1. Neutralistion of 100 ml. *N* HCl with *N* NaOH (calculated).

II. *Titration of a weak acid with a strong base:* In this case the product of the titration is a salt which is hydrolysed and furthermore the weak acid is not wholly dissociated. We have to consider the following equilibria:

$$A^- + H_2O \rightleftharpoons OH^- + HA;\ H_2O \rightleftharpoons H^+ + OH^-;\ HA \rightleftharpoons H^+ + A^-$$

We have:

$$K_h = \frac{[OH^-]\times[HA]}{[A^-]};\ K_w = [H^+]\times[OH^-] \text{ and } K_A = \frac{[H^+][A^-]}{[HA]}$$

The *concentrations of HA and OH^- formed due to hydrolysis* are equal. Taking C as the concentration (gm mols/litre) of the salt

we have:

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{K_w.C}{K_A.[OH^-]} \text{ so that } [OH^-] = \sqrt{C.K_w/K_A}$$

Again $$[H^+] = K_w/[OH^-] = \sqrt{K_w.K_A/C}$$

$$pH = \tfrac{1}{2}pK_w + \tfrac{1}{2}pK_A + \tfrac{1}{2}\log C$$

This relation is used for calculation of pH at the equivalence point and for other concentration the relation $pH = pK_A + \log [Salt]/[Acid]$ (page. 173. Part I) is used.

Taking the case of titration of 100 ml 0.1N acetic acid ($K_A = 1.82 \times 10^{-5}$; $pK_A = 4.74$) with 0.1N NaOH we have:

$$\frac{[H^+]\,[CH_3COO^-]}{[CH_3COOH]} = \frac{[H^+]^2}{[CH_3COOH]} = \frac{[H^+]^2}{0.1} = 1.82\times10^{-5}(\ = K_A)$$

$$\therefore \quad [H^+] \text{ at the start} = \sqrt{0.1\times1.82\times10^{-5}} = 1.35 \times 10^{-3};\ pH = 2.87.$$

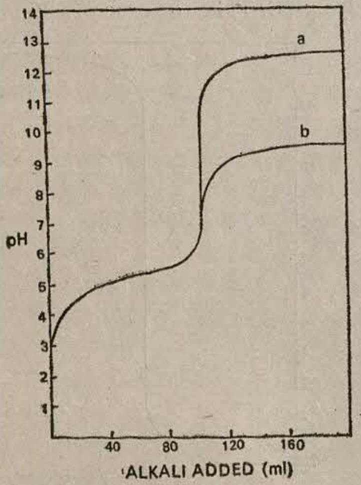


Fig. VI.2. Neutralisation curves of 100 ml 0.1N acetic acid with (a) 0.1N sodium hydroxide and (b) 0.1N ammonium hydroxide

When 50 ml 0.1N NaOH is added we have:

$$pH = 4.74 + \log \frac{(50\times0.1)/150}{(50\times0.1)/150} = 4.74$$

At the equivalence point $pH = \tfrac{1}{2}(14) + \tfrac{1}{2}(4.74) + \tfrac{1}{2}\log 0.05 = 8.72$. After the equivalence point pH will be dictated by the concentration of excess OH^- ion. Addition of 100.2 ml 0.1N NaOH will produce a pH 10.0$[OH^-] = (0.2 \times 0.1)/200.2 = 1\times10^{-4}$; $pOH = 4$; $pH = 10$). The major point that emerges is that in this titration pH changes rather slowly (8.5—10.0) near the equivalence point. If the acid is weaker than acetic acid (say $K_A \sim 10^{-7}$) the equivalence point pH will be shifted to still higher pH ~ 10. In such titration phenolphthalein, thymol blue or preferably thymolphthalein (which changes colour in the pH range 9.3—10.5) should be used as indicator. Remember methyl red or methyl orange will be bad choice.

III. Titration of a weak base with a strong acid:

We now have to consider the following equilibria:

$$M^+ + H_2O \rightleftharpoons MOH + H^+; \; MOH \rightleftharpoons M^+ + OH^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

The following relations hold:

$$K_b = \frac{[M^+]\,[OH^-]}{[MOH]}; \quad K_w = [H^+]\,[OH^-]$$

$$K_h = \frac{[H^+]\,[MOH]}{[M^+]} = \frac{[H^+]\,[OH^-]}{K_b} = \frac{K_w}{K_b}$$

Again [MOH] and $[H^+]$ are equal so that $K_h = \dfrac{[H^+]^2}{C} = \dfrac{K_w}{K_b}$ where C is the concentration of the salt in gm. mols/litre.

$$\therefore \quad [H^+] = \sqrt{C \,.\, K_w/K_b}$$

$$\therefore \quad pH = \tfrac{1}{2}\,pK_w - \tfrac{1}{2}\,pK_b - \tfrac{1}{2}\log C$$

This relation is used to calculate the pH at the equivalence point.

Consider the titration of 100 ml 0.1*N* aqueous ammonia ($K_b = 1.8 \times 10^{-5}$) with 0.1*N* HCl. The pH of the ammonium hydroxide solution at the start is computed as follows:

$$K_b = \frac{[OH^-]\,[NH_4^+]}{[NH_4OH]} = 1.8 \times 10^{-5}$$

$$\frac{[OH^-]^2}{[NH_4OH]} = \frac{[OH^-]^2}{0.1} = 1.8 \times 10^{-5} \qquad ([OH^-] = [NH_4^+])$$

$$\therefore \; [OH^-] = \sqrt{1.8 \times 10^{-6}}; \; pOH = 2.88 \text{ so that } pH = 11.12.$$

Again $[OH^-] = [NH_4OH]\,(K_b)/[NH_4^+]$

So that $pOH = \log [\text{Salt}]/[\text{Base}] + pK_B$

$$\therefore \quad pH = pK_w - pOH = pK_w - pK_B - \log[\text{Salt}]/[\text{Base}]$$

At the equivalence point we have

$$pH = \tfrac{1}{2}(14) - \tfrac{1}{2}(4.74) - \tfrac{1}{2}\log(0.05) = 5.28$$

After the equivalence point $[H^+]$ will dominate the pH so that when 100.2 ml 0.1*N* HCl is added we have:

$$[H^+] = (0.2 \times 0.1)/200.2 = 1 \times 10^{-4}; \; pH = 4.0$$

Around the equivalence point pH will change from ~ 6 to 4. (Fig. VI.3). It is imperative that methyl red, methyl orange or bromocresol green should be used as indicators in such titrations. Phenolphthalein, thymol blue are no choice whatsoever.

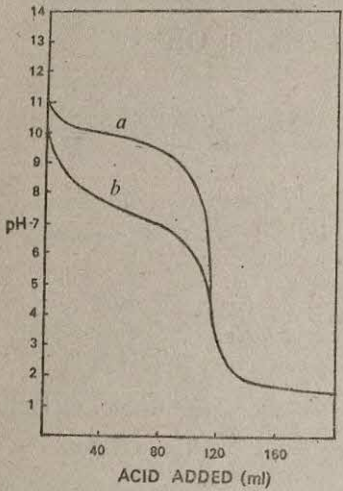


Fig. VI. 3 Neutralisation curves of (a) 100 ml 0.1*N* NH_4OH and of (b) a 0.1*N* base ($K_B = 1 \times 10^{-7}$) with 0.1*N* HCl.

IV Titration of a weak acid with a weak base: Here both the reactants are incompletely dissociated and the salt produced will also be hydrolysed.

The following equilibria are considered:

$$M^+ + A^- + H_2O \rightleftharpoons MOH + HA$$

$$HA \rightleftharpoons H^+ + A^-$$

$$MOH \rightleftharpoons M^+ + OH^-$$

$$K_A = \frac{[H^+]\,[A^-]}{[HA]}\,;\; K_B = \frac{[M^+]\,[OH^-]}{[MOH]}$$

$$K_w = [H^+]\,[OH^-]$$

$$K_h = \frac{[MOH]\,[HA]}{[M^+]\,[A^-]} = \frac{K_w \times K_B}{K_A}$$

If x is the degree of hydrolysis of 1 gm mol of the salt dissolved to make v litres of solution then we have:

$$[MOH] = [HA] = \frac{x}{v} \text{ and } [M^+] = [A^-] = \frac{1-x}{v}$$

so that $$K_h = \frac{x^2}{(1-x)^2}$$

Again $$[H^+] = K_A \times \frac{[HA]}{[A^-]} = K_A \times \frac{x}{1-x} = K_A \times \sqrt{K_h}$$

$$= \sqrt{(K_w \times K_A)/K_B}$$

Then $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_A - \frac{1}{2}pK_B$

Let us take the case of titration of 100 ml 0.1*N* acetic acid ($K_A = 1.8 \times 10^{-5}$; $pK_A = 4.74$) with 0.1*N* NH_4OH ($K_B = 1.8 \times 10^{-5}$; $pK_B = 4.74$). To start with the pH of the acetic acid is 2.87.

At the equivalence point we have:

$$pH = \tfrac{1}{2}(14) + \tfrac{1}{2}(4.74) - \tfrac{1}{2}(4.74) = 7.0$$

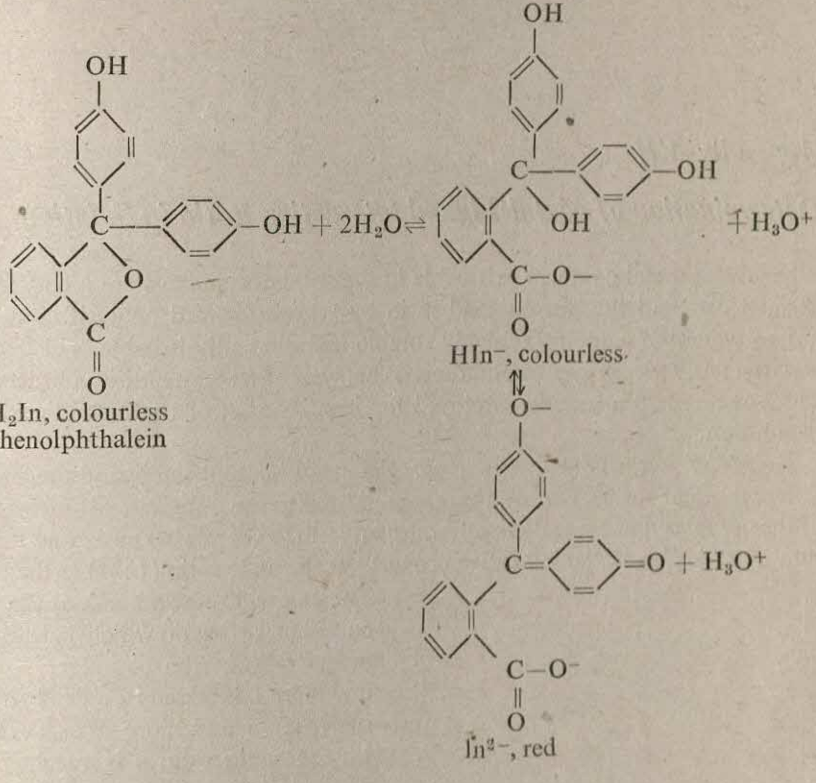
After the equivalence point the pH will be due to addition of aqueous ammonia to ammonium acetate. The equation:

$$pH = pK_w - pK_B - \log [\text{Salt}]/[\text{Base}]$$

can be used to calculate the pH. It will be evident that there is no sharp pH change during such titration. Indeed it is hard to find a suitable indicator for such titrations. The best course is to avoid such tiration.

Given below are the structures and colours of three widely used acid-base indicators: (a) phenolphthalein (b) methyl orange and (c) methyl red in acidic and basic media.

(a)

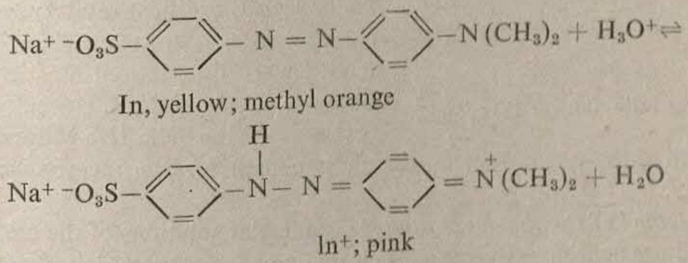


H$_2$In, colourless
phenolphthalein

HIn$^-$, colourless

In^{2-}, red

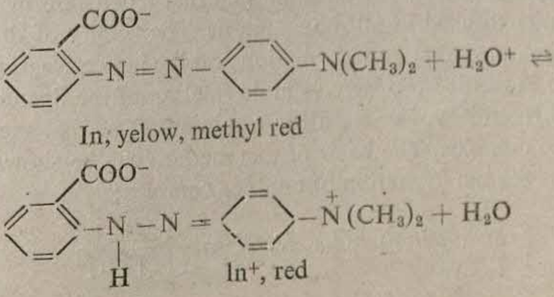
(b)


Na$^+$ $^-$O$_3$S–
– N = N –
–N(CH$_3$)$_2$ + H$_3$O$^+$ ⇌
H
–N– N =
= $\overset{+}{N}$(CH$_3$)$_2$ + H$_2$O

In, yellow; methyl orange

In$^+$; pink

(c)


COO$^-$
–N = N –
–N(CH$_3$)$_2$ + H$_3$O$^+$ ⇌
–N –N =
–$\overset{+}{N}$(CH$_3$)$_2$ + H$_2$O
H

In, yelow, methyl red

In$^+$, red

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Appendix VII

Determination of Metal-Ligand Interacting Ratio in Solution

Whenever a metal complex is isolable in the solid crystalline state a coordination chemist can find the metal-ligand ratio by straightforward analysis. But this is not so when the complex is highly soluble and difficultly isolable. This situation is particularly met in spectrophotometric analysis of trace quantities of metal ions. Three methods are usually employed for identification of the metal-ligand ratio in solution.

1. *Molar Ratio Variation Method:* The metal ion and the ligand are mixed in different molar ratios, the solutions are adjusted to the optimum pH of formation of the complex and some distinctive property of the complex is measured in all the solutions. A plot of the indicative property vs the mole ratio $(L{:}M)$ is then made. The plot will show a break at that particular $[L]:[M]$ ratio which is the interacting ratio in the complex. As more and more L is added to a fixed quantity of M, more and more ML_n is formed till the molar ratio n is reached. This method gives excellent result when the complex ML_n is a strong one i.e. its tendency to dissociation into the components is only minimal. Uusually optical density is the indicative property and the wave length of the absorption maximum is chosen for the measurement of optical density.

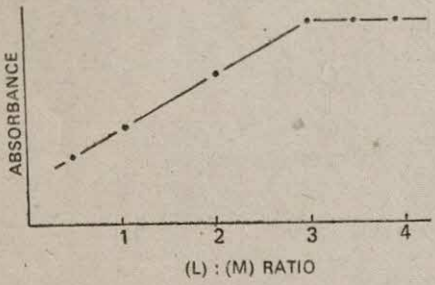

Fig VII.1. Molar ratio plot for 1:3 complex

2. *Job's Method of Continuous Variation:* Equimolar solutions of the metal ion and the ligand are continuously varied such that a constant metal ion plus ligand concentration is reached in all the solutions. The acidity of the solutions is then adjusted to the optimum pH of formation and the indicative property is measured. A plot of the indicative property vs mole fraction of the ligand i.e. the ratio $[L]/([M^{n+}] + [L])$ gives a maximum (or a minimum) at that metal-ligand ratio as obtains in the complex. The basis of this method can be shown by the following manipulations for the formation of an ML_n complex:

$$M + nL \rightleftharpoons ML_n \quad \therefore K = \frac{[ML_n]}{[M]\,[L]^n} \qquad \ldots (1)$$

$$\text{so that } [M]\ [L]^n = \frac{1}{K}[ML_n] \qquad \ldots (1a)$$

$$\text{total metal} = M_t = [M] + [ML_n] \qquad \ldots (2)$$

$$\text{total ligand} = L_t = [L] + n\,[ML_n] \qquad \ldots (3)$$

$$M_t + L_t = \text{constant} \qquad \ldots (4)$$

Differentiating with respect to $[L]$ we have :

$$\frac{d[M]}{d[L]}[L]^n + n[M][L]^{n-1} = \frac{1}{K}\,\frac{d[ML_n]}{d[L]} \qquad \ldots (5)$$

$$\frac{d[M_t]}{d[L]} = \frac{d[M]}{d[L]} + \frac{d[ML_n]}{d[L]} \qquad \ldots (6)$$

$$\frac{d[L_t]}{d[L]} = 1 + n\,\frac{d[ML_n]}{d[L]} \qquad \ldots (7)$$

$$\frac{d[M_t]}{d[L]} + \frac{d[L_t]}{d[L]} = 0 \ \text{ so that } \frac{d[M_t]}{d[L]} = -\frac{d[L_t]}{d[L]} \qquad \ldots (8)$$

When the complex goes to maximum $\frac{d[ML_n]}{d[L]}$ becomes zero so that

we have:

$$\text{from (5)}: n[M][L]^{n-1} = -\frac{d[M]}{d[L]}[L]^n \qquad \ldots (9)$$

$$\text{from (6)}: \frac{d[M]}{d[L]} = \frac{d[M_t]}{d[L]} \qquad \ldots (10)$$

$$\text{from (7)}: \frac{d[L_t]}{d[L]} = 1 \qquad \ldots (11)$$

$$\text{from (8)}: \frac{d[M_t]}{d[L]} = -\frac{d[L_t]}{d[L]} = -1 \qquad \ldots (12)$$

Combining (9) and (10) we have:

$$n[M][L]^{n-1} = -\frac{d[M_t]}{d[L]}[L]^n \qquad \ldots (13)$$

$$= [L]^n \text{ (from (12))} \qquad \ldots (14)$$

$$\text{Therefore} \qquad n = \frac{[L]^n}{[M]\,[L]^{n-1}} = \frac{[L]}{[M]} = \frac{[L_t] - n[ML_n]}{[M_t] - [ML_n]}$$

(from (2) and (3))

$$\text{Then } [L_t] - n[ML_n] = n[M_t] - n[ML_n] \qquad \ldots (15)$$

$$\therefore n = \frac{[L_t]}{[M_t]} \qquad \ldots (16)$$

Thus the metal-ligand interacting ratio is given by the ratio of the total ligand to the total metal ion in that particular solution where complex formation attains a maximum (Fig. VII.2). The complete formation side of the Job's curve gives us the molar indicative property of the complex. With this knowledge we can analyse the incomplete formation side to get the concentration of the complex formed, concentration of the free metal ion and the concentration of the free ligand. Thus the 'conditional stability constant' (K) can be evaluated (equation 1). Let us consider a particular solution on the complete formation side of the Job's plot. Let us further assume that the indicative property is absorbance (*i.e.* optical density) and neither the metal ion nor the ligand has any absorbance at the wave length the complex shows its maximum absorbance. If the measured optical density (at the chosen wave length) of a solution on the complete formation side is A and the known concentration of the metal ion is C then the molar absorbance of the complex is $A/C = x$. Now let us take a chosen solution on the incomplete formation part of the Job's plot. If the measured optical density is B then the concentration of the complex is $B/x = y$.

For a 1:1 complex $k = \dfrac{[ML]}{[M]\,[L]}$

We have $[ML] = y$; $[M] = M_t - y$;

$[L] = L_t - y$;

$$\therefore\ K = \frac{y}{(M_t - y)\,(L_t - y)}$$

For a 1:2 complex $K = \dfrac{[ML_2]}{[M]\,[L]^2}$

We have $[ML_2] = y$; $[M] = M_t - y$; $[L] = L_t - 2y$

$$\therefore\ K = \frac{y}{(M_t - y)\,(L_t - 2y)^2}$$

Such constants can also be evaluated from an analysis of the molar ratio variation plot. The usual indicative property is optical density. Use of other physical properties often gives trouble in connecting the variation of that property with the concentration of the different species.

3. *Slope Ratio Method:* When $[L]$ is large and constant but $[M]$ varies from solution to solution the equilibrium concentration of ML_n i.e.

$$M + nL \rightleftharpoons ML_n$$

$[ML_n]$ is given by the concentration of the metal ion C_M. Taking the indicative property to be optical density we know $A = abc$, where A is the optical density of the solution, a is the molar extinction coefficient, b is the cell path length and c is the concentration of the coloured species. Then $A = ac = a\,[ML_n] = aC_M$ ($b = 1$ cm). A plot of A vs C_M will be a straight line with a slope a. Similarly concentration of M may be kept very large while the concentration of L i.e. C_L is varied. Then we have: $A = a\,[ML_n]$. But $[ML_n] = C_L/n$ so that $A = (a/n)C_L$.

A plot of A vs. C_L will give another straight line with a slope (a/n). The ratio of the two slopes gives n.

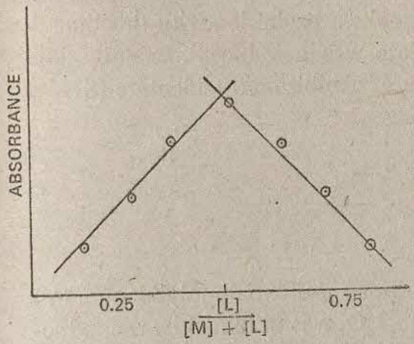

Fig. VII. 2 Job's plot for 1 : 1 complex.

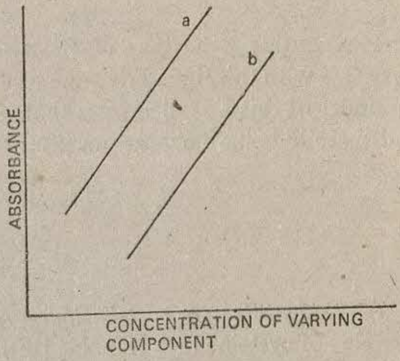

Fig. VII.3. Slope ratio plot for 1 : 1 complex; one of the plot is for metal varying (reagent constant) and the other for reagent varying (metal constant).

The reader should appreciate that such empirical composition determination does not tell us anything about the coordination number of the metal ion or the stereochemistry.

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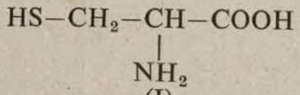
Appendix VIII

Flexidentate Behaviour of Polydentate Ligands

I. Introduction—A flexidentate ligand[1] is one that can chelate a metal ion in more than one way. Since metal chelation is the result of donor-acceptor interaction it can be understood easily that flexidentate behaviour will be dictated by the following factors: (*a*) preference for a particular coordination number by a metal ion (b) competition by two or more ligands for suitable coordination sites around the metal ion (*c*) preference of the metal ion for certain chromophores and (*d*) pH during formation of the complex, particularly when the flexidentate ligand has donor groups of different acid character.

Identification of the flexidentate behaviour is usually made by (*a*) electronic spectra of the complex (*b*) infrared spectra and (*c*) proton magnetic resonance spectra. In the case of a crystalline complex (where single crystal can be grown) a thorough X-ray crystallographic analysis unequivocally demonstrates the donor atoms around the metal ion and provides an evaluation of the various bond lengths and bond angles.

II. Flexidentate Behaviour of Cysteine (I)—We make a beginning with this ligand (I) as it is with this ligand that the term, flexidentate, was introduced[1]. Examination of model of this ligand reveals that it is capable of exhibiting a tridentate (SNO) and three bidentate characters (SN, NO, SO)

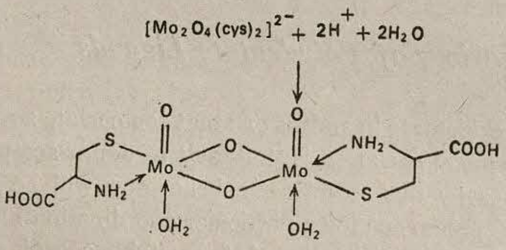


$$HS-CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH$$

(I)

A. *Tridentate SNO Behaviour*—A dimeric di-oxo μ-dioxo dimolybdenum (V) complex of cysteine (cys H_2) $Na_2[Mo_2O_4(cys)_2]5H_2O$, was obtained by the reduction of aqueous solution made from sodium orthomolybdate (Na_2MoO_4) and cysteine hydrochloride with hydrazine or sodium dithionite[2]. An alternative synthesis involved reacting $MoCl_5$ in $3N$ HCl with a 3:1 excess of crysteine hydrochloride[3]. The solution was then neutralised with NaOH and ethanol was used to facilitate crystallisation of the sodium salt. The complex is diamagnetic (μ = 0.53 B.M. at 25°C) indicating strong antiferromagnetic (metal-metal) interaction between the two molybdenum (V) atoms ($4d^1$). The structure of the complex has been solved through single crystal X-ray analysis[4]. The major bond lengths are: Mo–O(terminal) = 1.71 A; Mo–O (bridging) = 1.92 A; Mo–Mo = 2.57 A; Mo–O(cysteine) = 2.30 A; No–N (cysteine) = 2.23 A; Mo–S(cysteine) = 2.49A. It is thus established that in this complex the cysteine ligand uses all its three donor centres (SNO) for coordination to molybdenum (V).

B. Bidentate SN Behaviour—It is of interest to note that at lower pH the above dimeric complex undergoes protonation[5] of its coordinated $-COO^-$ to $-COOH$. This protonation weakens the coordinating property of the ligand and thus the $-COOH$ group is displaced from the coordination site by H_2O molecules:



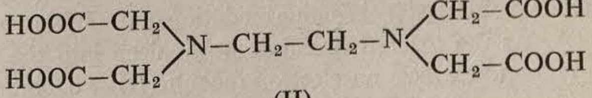
This complex was subjected to pH titration which gave pK_a values of 2.03 and 4.07 for ionisation of the two protons. These values are considered reasonable as the pK_a for carboxylate ionisation of free cysteine[6] is around 2. Thus we find that the above diaquo complex has two bidentate cysteines coordinating as SN donors.

Reaction[1] of *trans*-$[Co(en)_2Cl_2]Cl$ (en = ethylenediamine) with L-cysteine in the presence of NaOH at 60°C led to the formation of a dark brown product which was isolated as the iodide salt: $[\mathrm{Co(en)_2(cys)}]\mathrm{I.H_2O}$. Molecular weight and conductance data identified the product as a uni-univalent electrolyte. The i.r. spectrum betrayed no band around 2500 cm^{-1} (S-H stretch[7]) suggesting that the mercaptide group is coordinated to the central metal ion. An intense C = O stretch is observed at 1616 cm^{-1} indicating that the complex has an uncoordinated carboxylate group. A confirmation of this is provided by the presence of a band at around 1600 cm^{-1} for a nitrogen coordinated (monodentate) amino acid group in the mixed ligand complex[8] $[\mathrm{Co(en)_2(NH_2CH_2COO)Cl}]\mathrm{Cl}$. The free carboxylic acid group of glycine has a band at 1735 cm^{-1}. That the $\mathrm{NH_2}$ group of cysteine is coordinated to cobalt (III) is supported by the lowering of the two primary amine bands (3100–3200 cm^{-1}) by about 100 cm^{-1}.

C. Linkage Isomerism[9] *in tris(cysteinato)cobalt(III)*—This complex has been obtained in two differently coloured isomeric forms: (*a*) red variety and (*b*) green variety. The red isomer was obtained by air oxidation of a mixture of cobalt (III) and cysteine at pH 5-6. This isomer has cysteinate anion coordinated to cobalt (III) through S and O donor atoms. The electronic spectrum was found to be very similar to that of the complex tris(3-mercaptopropionato)cobalt(III). The red complex changed to the green form on treating with hot sodium cysteinate at pH 12. That the donor centres are N and S has been deduced from a comparison of the spectrum with that of the cobalt (III) complex of 2-amino-ethane thiol.

D. Bidentate NO Behaviour[10]—The bidentate NO behaviour has been inferred from potentiometric study of the calcium (II) complex $[\mathrm{Ca(cysH)(H_2O)_4}]^{2+}$. Similar behaviour has also been proposed for the mixed complex containing a bidentate cysteine, a tridentate dipicolinate ligand and a molecule of water: $[\mathrm{Ca(H_2O)\,(dipic)\,(cysH)}]^-$.

III. Flexidentate behaviour of ethylenediaminetetraacetic acid (II)—This ligand (II) is all too well-known as an excellent complexometric titrant for estimation of water hardness as well as for estimations of several other metal ions like zinc (II), nickel (II), iron (III) etc[11]. Although the ligand is potentially sexadentate it has also been shown to function as pentadentate (NNOOO), quadridentate (NNOO), as bidentate (NN) chelating agent and finally as a bridging (OON–NOO) sexadentate.



$$\begin{array}{l}\mathrm{HOOC-CH_2}\\ \mathrm{HOOC-CH_2}\end{array}\!\!>\mathrm{N-CH_2-CH_2-N}<\!\!\begin{array}{l}\mathrm{CH_2-COOH}\\ \mathrm{CH_2-COOH}\end{array}$$

(II)

A. Sexadentate behaviour—Following on the suggestion of Brintzinger et. al[12] structure analyses of several isomorphous series $\mathrm{M^I\ [M^{III}\ (EDTA)].\ 2H_2O}$ ($\mathrm{M^I = NH_4^+,\ Rb^+,\ M^{III} = Co^{III},\ M^I = NH_4^+,\ M^{III} = Cr^{III} = Al^{III}}$) have been carried out[13]. The cobalt (III) ion in $[\mathrm{Co(EDTA)}]^-$ is bonded octahedrally to the two nitrogen atoms and to one oxygen atom from each of the four carboxylate groups of the ligand. The ligand has as many as five chelating rings, of which three (including the $-N-CH_2-CH_2-N-$) rings encircle the cobalt (III) ion as a girdle. The other two rings are at right angles to each other. An examination of model also reveals this pattern when EDTA anion functions as a sexadentate ligand. In keeping with these structural findings it has been observed that the free, uncoordinated carboxylic acid group frequency at $\sim$ 1740 cm^{-1} is absent in the above salts of $[Co(EDTA)]^-$, $[Cr(EDTA)]^-$ and $[Al(EDTA)]^-$ but is replaced by a band at $\sim$ 1638 cm^{-1}. Cobalt (III) EDTA complex serves as a good example of inert i.e. non-labile metal-ligand bonds. The acetate groups in $[Co(EDTA)]^-$ exist as two non-equivalent pairs. Two acetate groups are in the ethylenic nitrogen-to-cobalt (III) plane and are thus equivalent. But the other two acetate groups are out of this plane and are equivalent to each other. The two methylene protons on a given acetate group are in different magnetic environments and give rise to an AB pattern in the pmr spectrum. It is likely that two types of acetate groups will provide two AB patterns. It is also not entirely unlikely that the rigidity of the structure of the complex may make the ethylenic protons non-equivalent. The actual spectrum of $[Co(EDTA)]^-$ run in aqueous medium shows two AB patterns besides some peaks due to the highly split ethylenic protons within the range of δ = 3.5 to 4.5 ppm with respect to TMS as the standard.[14]

B. Pentadentate behaviour—There are several examples of EDTA complexes where this amino polycarboxylic acid ligand is known to take up five coordination positions about a metal ion. X-ray crystallographic analyses[15] of the green $[Ni(H_2O)(H_2EDTA)]$ and the blue $[Cu(H_2O)(H_2EDTA)]$ show that the ligand is pentadentate. The octahedral geometry about copper (II) and nickel (II) is completed by the aqua molecule. One acetate group keeps away from the sixth coordination site. The aqua molecule lies in the equatorial position and is *cis* to one nitrogen but *trans* to the other nitrogen.

Chromium (III) reacts with EDTA to form a violet $[Cr(EDTA)]^-$ where the ligand is six-coordinate. This violet complex (λ_{max} = 545 nm) can be spectrophotometrically titrated to give a blue complex (λ_{max} = 600 nm). A distinct break[16] is observed at 1:1 $[Cr(EDTA)]^-$: OH^- indicating the formation of $[Cr(OH)(EDTA)]^{2-}$. This complex ion containing pentadentate EDTA has also been successfully isolated in the solid state as bis(biguanide)copper (II) salt[17]: $[Cu(BigH)_2]$ $[Cr(OH)(EDTA)]$.

Schwarzenbach[18] has reported a long series of salts of $[Co(Br)(EDTA)]^{2-}$. The complex anion was obtained by bromine oxidation of a solubion of a cobalt (II) complex of EDTA. As the oxidant bromine moves deep into the coordination sphere of cobalt (II) and extracts an electron (cobalt (II) → cobalt (III)) it gets reduced to bromide ion. The latter is immediately trapped as a ligand around cobalt (III) with the result that one of the carboxylate groups withdraws to make room for the bromide ligand.

Maki[18a] has prepared $Na_2[Co(CN)(EDTA)]$ by treating *trans*-$[Co(CN)(NH_3)_4I]I$ with Na_4EDTA. The infrared spectral data indicate that EDTA functions as a pentadentate ligand in the complex.

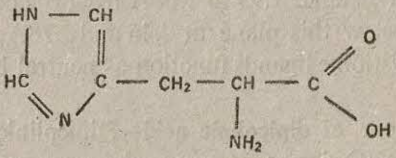
C. Quadridentate behaviour—The platinum (II) and palladium (II) complexes of quadridentate EDTA[19] are most conveniently prepared from the corresponding complexes having bidentate EDTA (as described in IIID below). The reaction is carried out by neutralisation of two of the four carboxyl groups of [Pd/Pt(H_4EDTA)Cl_2] and simultaneous removal of the coordinated chloride groups with silver ion. The products are isolated as the free acid [Pd/Pt(H_2EDTA)]. The free COOH bands show up at ~ 1730 cm^{-1} while the coordinated COO^- bands appear at 1635 cm^{-5}.

D. Bidentate behaviour—Disodium dihydrogen ethylenediaminetetraacetic acid reacts with $PtCl_2$, $PdCl_2$, K_2PtCl_4 and K_2PdCl_4 to form complexes which are obtained from concentrated HCl as bright crystals having the composition[19] [Pd/Pt(H_4EDTA)Cl_2]. pH titration produces an equivalent weight of 141.9 (calc. 140) for the platinum (II) complex. That all the four COOH groups are uncomplexed and that EDTA is linked to Pd/Pt through the two nitrogen atoms is revealed by very strong split carbonyl bands observed at 1707 and 1730 cm^{-1} for the palladium(II) complex and at 1715 and 1730 cm^{-1} for platinum(II) complex.

E. Bridging sexadentate behaviour— The dinuclear di-μ EDTA dimolybdenum (V) complex[20] $Na_2[Mo_2O_4(EDTA)]$ H_2O has been obtained by neutralisation of Mo (V) EDTA solution (molybedenum(V) being obtained by reduction of molybdenum (VI) with mercury in 3*N*HCl). A study of the model of this compound shows that a stable structure results with the two EDTA nitrogens occupying positions *trans* to the two terminal oxygens of the two molybdenum (V).

Another example[21] of bridging by EDTA is observed in the dimeric molybdenum(VI) complex $Na_4[O_3Mo(EDTA)MoO_3].8H_2O$. A complete structural analysis shows that EDTA binds to each MoO_3 unit through an amino nitrogen and the two carboxylato oxygens that spring from that particular nitrogen. The ethylenediamine backbone holds in position the two halves of the dimeric complex. The structure further reveals that all the O_3Mo oxygens are terminal and that there are no Mo—O—Mo— or direct Mo—Mo links.

IV. Flexidentate behaviour of histidine—This amino acid (III, histH) with an imidazole moiety can function potentially as a tridentate (NNO) donor, a bidentate (NN) donor or as a bidentate (NO) donor.



(IIII)

A. *Tridentate NNO behaviour*—Bis (L-histidinato) cobalt (II) was synthesised as pink needles from the reaction of cobalt carbonate and histidine in boiling water and then allowing to crystallise in a sealed tube. Such precautions did not allow the cobalt (II) complex to absorb moisture, which it otherwise does. The structure[22] of this bis(L-histidinato) cobalt (II) monohydrate has been solved via three dimensional X-ray diffraction. The cobalt (II) atom is octahedrally coordinated to the amino-nitrogen, an imidazole nitrogen and an oxygen atom of each histidine group, at distances between 2.10 and 2.20A.

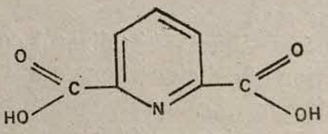
Following the above procedure but using DL histidine Candlin and Harding[23] obtained (D-histidinato) (L-histidinato) cobalt (II) dihydrate. Its structure is very similar to the one described above. The cobalt (II) is in an octahedral surrounding of amine nitrogen, imidazole nitrogen and an oxygen atom of the carboxylic group of each histidine molecule. The cobalt-donor atom distances are in the range 2.06–2.16A.

A dimeric dioxo μ-dioxo di(histidinato) di (molybdenum (V)) complex $[Mo_2O_4(hist)_2]$ has also been synthesised and structurally characterised[24]. The ligand functions as NNO tridentate donor. The structure is very close to that of the cysteine analogue, described in section IIA.

B. Bidentate NN behaviour—Since cobalt(III) is consistently six-coordinate in its complexes the syntheses and elucidation of the structure of the mixed chelate $[Co(hist)(BigH)_2]^{2+}$ (BigH= bidentate biguanide) alongwith the chelates $[Co(AB)(BigH)_2]^{2+}$ (ABH = glycine, α-alanine, 1-leucine etc.) were undertaken[25]. All these mixed chelates were prepared by the action of histidine or the amino acids on *cis*-$[Co(NH_3)_2(BigH)_2]^{3+}$ and isolated as halide salts. While the histidinato bis(biguanide)cobalt (III) was orange red ($^1A_{1g} \rightarrow {}^1T_{1g}$ transition at 21.1 kK) all the other aminoacidatobis(biguanide)cobalt (III) complexes looked red-violet ($^1A_{1g} \rightarrow {}^1T_{1g}$ transition at 20.41 kK). A comparison of the first transition of $[Co(hist)(BigH)_2]^{2+}$ with several other cobalt (III) chromophores ($[Co(BigH)_3]^{3+}$, 21.1 kK, $[Co(en)_3]^{3+}$, 21.5 kK; $[Co(dipy)(BigH)_2]^{3+}$, 21.4 kK; $[Co(o\text{-}phen)(en)_2]^{3+}$, 21.5 kK) indicates that histidinate ion behaves as an NN bidentate donor using the imidazole nitrogen and the amino-nitrogen (en = ethylenediamine, dipy = α, α'-dipyridyl, o-phen=o-phenanthroline).

C. Bidentate NO behaviour—Crystal structure determination[26] of bis (L-histidine) copper (II) nitrate dihydrate has revealed that both the L-histidine molecules are coordinated to the central copper atom through the amino nitrogen and the carboxylic oxygen. The imidazole groups are not coordinated to the copper atom and turn away from it. The coordination about copper (II) is square planar with the four donor atoms at a distance 1.93 to 2.00A from the copper. The two H_2O molecules lie above and below this plane at 2.46 and 2.78A. It is to be noted that in this complex the two histidine ligands function as neutral bidentate donors.

V. Flexidentate behaviour of dipicolinic acid—Dipicolinic acid* ($dipicH_2$, IV) is potentially tridentate ONO donor. However there are several instances where the ligand functions as a bidentate NO donor under forcing conditions.



(IV)

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* also known as lutidinic acid, Lut H_2,

A. Tridentate ONO behaviour—The ligand is known to react with vanadyl sulphate in aqueous medium to give beautiful needles[27] of $[VO(dipic)(H_2O)_2]H_2O$. As demanded by electroneutrality and stereochemistry of oxovanadium(IV) the complex does not betray the free carboxylic stretch around 1720 cm^{-1} but strong, sharp band at 1625 cm^{-1}. Several mixed chelates of the type [VO(dipic) (acacH)], [VO(dipic) (glyH)] (acacH = acetylacetone, glyH = glycine) etc. have also been characterised[27].

A bipositive silver (II) complex[28] $[Ag(dipic)(dipicH_2)]$ has been obtained as red crystals by peroxydisulphate oxidation of silver (I) in presence of excess dipicolinic acid. A thorough crystallographic study[28] reveals that silver (II) is octahedrally surrounded by a di-deprotonated dipicolinate ligand and a dipicolinic acid. The bonding parameters are: for the dipic ligand—Ag—N = 2.09 A, Ag—O ≐ 2.20A and 2.20A, for the $dipicH_2$ coordination—Ag—N = 2.21A, Ag—O—2.53A and 2.53A.

A mixed chelate $[Co(den)(dipic)]^+$ (den = diethylenetriamine) has also been synthesised and studied[29].

B. Bidentate NO behaviour[30,31]—Reaction of picolinic acid (picH) and dipicolinic acid with *cis*-$[Co(NH_3)_2(BigH)_2]^{3+}$ produced $[Co(pic)(BigH)_2]^{2+}$ and $[Co(dipic)(BigH)_2]^+$ respectively. The first electronic transition ${}^1A_{1g} \rightarrow {}^1T_{1g}$ appears at 20.6 kK and 20.5 kK for the above two complexes. The similarity in the spectra points to the fact that both the complexes have the same chromophore $[CoN_5O]$ i.e. dipicolinic acid functions in this mixed chelate as a bidentate NO donor. More recently reactions of dipicolinic acid with $[Cr(BigH)_3]^{3+}$, $[Cr(tu)_2(dipy)_2]^{3+}$ and $[Cr(tu)_2(o\text{-}phen)_2]^{3+}$ (tu = thiourea) have been observed to give blue-violet coloured [Cr(BigH) (dipic) (dipicH)], [Cr (dipy) dipic) (dipicH)] and [Cr(o-phen) (dipic) (dipicH)]. Since biguanide, dipyridyl and o-phenanthroline are known to function only as bidentate neutral donors and since chromium (III) is normally six-coordinate the only reasonable conclusion is that the dipic and dipicH ligands are coordinated to the metal ion as bidentate ligands. Conductance and pH measurements indicate some dissociation of the proton of the dipicH ligand. That such dissociation is expected to lead to some anionic character in the complex has been verified by their response to anion exchange resin. Several runs of the same solution through a column of IRA-400 (Cl^-) provides a colourless eluate. These eluates give good values for the equivalent weights of the three complexes on alkalimetric titration.

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Appendix IX

Molar Conductance Range for Various Electrolytes

Solvent	Charge type	Concentration	Molar conductance Range ohms^{-1} cm^{2}mole^{-1}
Water	1 : 1 (two ions)	0.001*M*	95–115
	2 : 1 (three ions)	0.001*M*	222–265
	3 : 1 (four ions)	0.001*M*	380–430
	4 : 1 (five ions)	0.001*M*	520
Methanol	1 : 1 (two ions)	0.001*M*	80–115
	2 : 1 (three ions)	0.001*M*	160–220
	3 : 1 (four ions)	0.001*M*	290–350
	4 : 1 (five ions)	0.001*M*	450
Acetonitrile	1 : 1 (two ions)	0.001*M*	120–160
	2 : 1 (three ions)	0.001*M*	220–300
	3 : 1 (four ions)	0.001*M*	340–420
	4 : 1 (five ions)	0.001*M*	500

Dimethylformamide	1 : 1 (two ions)	0.001*M*	65–90
	2 : 1 (three ions)	0.001*M*	130–170
	3 : 1 (four ions)	0.001*M*	200–240
	4 : 1 (five ions)	0.001*M*	300
Nitromethane	1 : 1 (two ions)	0.001*M*	75–90
	2 : 1 (three ions)	0.001*M*	150–180
	3 : 1 (four ions)	0.001*M*	220–260
	4 : 1 (five ions)	0.001*M*	290–330
Nitrobenzene	1 : 1 (two ions)	0.001*M*	20–30
	2 : 1 (three ions)	0.001*M*	50–60
	3 : 1 (four ions)	0.001*M*	70–82
	4 : 1 (five ions)	0.001*M*	90–100

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Appendix X

The Standard International (SI) Units

For the sake of doing justice to the latest thinking in the international area we give below the SI units alongside the more commonly used old units.

Table IX-1. Old units and the SI units

Physical quantity	*Old unit*	*Value in SI unit*
Energy	Calorie (thermochemical)	4.184J (Joule)
	*electron volt—*ev*	1.602×10^{-19}J
	*electron volt per mole	96.48 kJ mol^{-1}
	erg	10^{-7}J
	*wave number—cm^{-1}	1.986×10^{-23}J
Force	dyne	10^{-5}N(newton)
Pressure (P)	atmosphere	1.013×10^{5}Pa(pascal) or N m^{-2}(m = metre)
Dipole moment(μ)	Debye—D	3.334×10^{-30}Cm(C=Coulomb)
Frequency (v)	cycle per second	1 Hz (hertz)
Temperature (T)	*°C and°K	1 K(kelvin);0°C =273.2K

(* indicates permitted non-SI unit)

Table IX-2. Fundamental Constants in Old units and SI units

Fundamental Constants	*Value in Old units*	*Value in SI units*
Avogadro number/ constant	$L/N_A = 6.0225 \times 10^{23}\ \text{mol}^{-1}$	$6.0225 \times 10^{23}\ \text{mol}^{-1}$
Bohr radius	$a_0 = 0.529 \times 10^{-8}\text{cm}$	$0.529 \times 10^{-10}\text{m}$ (metre)
Boltzmann constant	$k = 1.3805 \times 10^{-16}\text{ergdeg}^{-1}$	$1.3085 \times 10^{-23}\text{JK}^{-1}$
Charge of an electron	$(-)4.803 \times 10^{10}$ esu	$(-)\ 1.602 \times 10^{-19}\text{C}$ (Coulomb)
Faraday	$F = 96{,}487$ colomb. g equiv^{-1}	$9.6487 \times 10^{4}\text{C mol}^{-1}$
Gas constant	$R = 1.9872\ \text{cal deg}^{-1}\ \text{mol}^{-1}$ $= 0.082057$ litre atm $\text{deg}^{-1}\ \text{mol}^{-1}$	$8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$
Planck constant	$h = 6.6256 \times 10^{-27}\text{erg.sec}$	6.6256×10^{-34} Js
Velocity of light in vacuum	$c = 2.99795 \times 10^{10}\text{cm sec}^{-1}$	$2.99795 \times 10^{8}\text{m sec}^{-1}$

Note the following conversion factors:

1 calorie = 4.184 J : 1 K cal = 4.184 kJ

1 dyne = 10^{-5} N

1 erg = 2.39×10^{-8} cal = 10^{-7} J

1 ev = $8066\ \text{cm}^{-1} = 23.06\ \text{Kcal mol}^{-1} = 1.602 \times 10^{-12}\ \text{erg} = 1.602 \times 10^{-19}\text{J}$

1 amu = 931.5 Mev = 1.66×10^{-24} erg = 1.66×10^{-31}J

1 cm^{-1} = 1.986×10^{-23}J

We give below a few sample examples of these transformations of units which are relevant to the discussions made in this book:

1. *Ionisation potential* : *cf* : *Part I* : *page* 70

First I.P. of Mg = 7.64 ev per Mg atom

= $7.64 \times 1.602 \times 10^{-19} \times 6.02 \times 10^{23}$J per mole of Mg atoms

= 7.4×10^{5}J per mole of Mg atoms

Second I.P. of Mg = 15.03 ev per Mg^{1+} ion

= 14.5×10^{5}J per mole of Mg^{1+} ions

II. *Bond Energies : cf : Part I : page* 80

Bond	*Energy in K Cal/mole*	*Energy in kJ/mole*
C − C	83	$83 \times 4.184 = 347$
C = C	143	598
C ≡ C	196	820
N − N	38	169
N ≡ N	225	941
C − O	84	351
C = O	173	724

III. *Dipole Moments : cf : Part I : page* 113

$$1 \text{ Debye} = 10^{-18} \text{ esu cm} = 10^{-18}\text{esu } 10^{-2}\text{m (metre)}$$

$$= \left(\frac{10^{-18}}{3\times10^{9}}\right) \text{C (Coulomb)} \times 10^{-2}\text{m [1 Coulomb} = 3\times10^{9} \text{ esu],}$$

$$= 3.334\times10^{-30}\text{C m}$$

Thus : $0.20 \text{ Debye} = 0.666\times10^{-30} \text{ C m}$
$1.86 \text{ Debye} = 6.201\times10^{-30} \text{ C m}$

IV. *Electronic Transition Energy: cf : Part* I *: page* 277

$11{,}000\text{cm}^{-1} = 1{,}1\times10^{4}\times1.986\times10^{-23}\text{J} = 2.184\times10^{-19}\text{J}$
$12{,}300\text{cm}^{-1} = 1.23\times10^{4}\times1.986\times10^{-23}\text{J} = 2.443\times10^{-19}\text{J}$
$18{,}500\text{cm}^{-1} = 1.85\times10^{4}\times1.986\times10^{-23}\text{J} = 3.674\times10^{-19}\text{J}$
$30{,}000\text{cm}^{-1} = 3\times10^{4}\times1.986\times10^{-23}\text{J} = 5.958\times10^{-19}\text{J}$

Addenda and Corrigenda

Part I

Page 20. *At the end*

Problem: The normal ionisation potential of hydrogen atom is 13.6 *ev*. What will be the value of the ionisation potential when the electron is raised to the 2*s* orbital?

The normal ionisation ionisation potential of hydrogen atom is the energy required to shift the electron from the 1*s* orbital to infinity and is given by the following expression:

$$\mathrm{E}_H = \frac{2\pi^2 me^4}{h^2}\left(\frac{1}{n_I^2} - \frac{1}{n_{II}^2}\right) = 13.6\ ev$$

where n_I refers to the 1*s* orbital from which the electron is withdrawn and n_{II} refers to infinity. For the excited hydrogen atom n_I is 2. So the ionisation potential for the removal of the electron from the 2*s* orbital to infinity:

$$E_H = 13.6\left(\frac{1}{2^2} - 0\right) = 13.6/4 = 3.4\ ev$$

Problem: Calculate the second ionisation potential of helium (given ionisation potential of hydrogen = 13.6 *ev*)

The ground state electronic configuration of helium is $1s^2$. The second ionisation potential means removal of the second electron from the 1*s* orbital against the nuclear charge of + 2. So we have:

$$\text{I.P.} = \frac{2\pi^2 mZ^2e^4}{h^2}\left(\frac{1}{n_I^2} - \frac{1}{n_{II}^2}\right) = Z^2 E_H$$

$$= 2^2 \times 13.6\ ev = 54.4\ ev$$

Problem: Which of the Balmer lines fall in the visible region of the spectrum (wave length 4000 to 7000 *A*) (given $R = 109,737\ \text{cm}^{-1}$).

The Balmer series of the hydrogen spectrum comprise the transition from $n > 2$ levels to the $n = 2$ level.

$$4000\,A = 4000 \times 10^{-8}\ \text{cm} = 4 \times 10^{-5}\ \text{cm}$$

$$7000\,A = 7 \times 10^{-5}\ \text{cm}$$

Therefore wave number $\bar{\nu} = \frac{1}{\lambda} = (\frac{1}{4}) \times 10^5$ to $(1/7) \times 10^5\ \text{cm}^{-1}$

Transition energy of the Balmer lines:

$$= \bar{\nu} = R\,(\text{in cm}^{-1})\left(\frac{1}{n_I^2} - \frac{1}{n_{II}^2}\right)$$

Taking $\bar{\nu} = (\frac{1}{4}) \times 10^5\ \text{cm}^{-1}$ we have:

$$(\tfrac{1}{4}) \times 10^5\ \text{cm}^{-1} = 109{,}737\ \text{cm}^{-1}\left(\tfrac{1}{4} - \frac{1}{n_{II}^2}\right) \simeq 1.1 \times 10^5\left(\tfrac{1}{4} - \frac{1}{n_{II}^2}\right)$$

$\therefore \frac{1}{4} \simeq 1.1\left(\frac{1}{4} - \frac{1}{n_{II}^2}\right)$; $n_{II}^2 \simeq 44$ so that $n_{II} \simeq 7$ (nearest whole number).

Taking the other case we have:

$$(1/7) \times 10^5\ \text{cm}^{-1} \simeq 1.1 \times 10^5\ \text{cm}^{-1}\left(\tfrac{1}{4} - \frac{1}{n_{II}^2}\right)$$

$1/7 \simeq 1.1\left(\frac{1}{4} - \frac{1}{n_{II}^2}\right)$ whence $n_{II}^2 \simeq 7.2$; $n_{II} = 3$ (nearest whole number).

So all transitions from $n = 7$ to $n = 3$ while falling to the $n = 2$ will generate the Balmer lines.

Problem: Calculate the energy of an electron in the Bohr orbit with $n = 3$. For the hydrogen atom the energy is;

$$E = -\frac{2\pi^2 me^4}{n^2h^2} = \frac{E_{(n=1)}}{n^2}$$

The value of $E_{(n=1)}$ is 13.6 *ev*. Hence the energy of the electron in the specified Bohr orbit is $-(13.6\ ev/3^2) = -1.5\ ev$.

This means that the 3*s* electron in the excited hydrogen atom is bound to the nucleus by an energy of 1.5 *ev* only.

Problem: Calculate the shortest wave length in the absorption spectrum of deuterium (given $R = 109{,}737\ \text{cm}^{-1}$)

Shortest wave length means highest energy and frequency. The deuterium case is comparable to the hydrogen case as in both the cases there is a single proton and single electron. Hence for the highest energy case we can write:

$$\bar{\nu} = R\left(\frac{1}{1^2} - \frac{1}{a^2}\right) = 109,\,737\ \text{cm}^{-1} = R$$

$$\text{wave length } \lambda = \frac{1}{\bar{\nu}} = \frac{1}{109,\,737\ \text{cm}^{-1}} = 0.911 \times 10^{-5}\ \text{cm}$$

$$= 0.911 \times 10^3 \times 10^{-8}\ \text{cm} = 911\ A$$

Problem: Calculate the first Bohr radius of He^+.

He^+ is comparable to hydrogen atom in having a single electron in its orbit but it has a nuclear charge $Z = 2$. For a general hydrogen like case with charge Z the radius is given by:

$$r = \frac{n^2h^2}{4\pi^2 mZe^2} = \frac{n^2 a_0}{Z} = \frac{1^2\,a_0}{2} = \frac{0.529\,A}{2} = 0.264\,A$$

Problem: The energy for the transition of the hydrogen electron from level 1 to 2 is 235.2 Kcal/mole while that for the transition from the level 4 to 5 is only 7.1 Kcal/mole. Why does it require more energy to activate an electron from the ground state to the next higher level than from a higher level to the next higher level?

The energy expression is $E = -\dfrac{2\pi^2 me^4}{n^2h^2} = \dfrac{E_{(n=1)}}{n^2}$

where $E_{(n=1)}$ is the ground state energy of the hydrogen atom. As the value of n in the denominator increases the negative E of the excited state rapidly decreases because of the square term. This means as the quantum number n increases the hydrogen electron becomes progressively unstable i.e. the binding energy of the electron progressively decreases. Hence we need less and less of energy to excite the hydrogen electron from one high quantum number to the next higher quantum number. Qualitatively as we move farther out of the nucleus the electron binding energy is bound to decrease.

Problem: A radiation of wave length 2000 A falls on a metal surface. Calculate the velocity of the electron ejected from the metal surface given that the minimum energy required for such ejection is 5 *ev*.

Einstein photoelectric effect is expressed as:

$$h\nu = h\nu_0 + \tfrac{1}{2}mv^2$$

where ν_0 and ν are the minimum frequency required for ejection and the actual frequency respectively. v is the velocity with which the electron is ejected.

The minimum energy required $= 5\ ev = 5 \times 8066\ \text{cm}^{-1} = 40{,}330\ \text{cm}^{-1}$

Thus $\nu_0 = c/\lambda_0 = c\bar{\nu}_0 = 3 \times 10^{10}\ \text{cm sec}^{-1} \times 40{,}330\ \text{cm}^{-1}$

$$= 3 \times 10^{10} \times 40{,}330\ \text{sec}^{-1} = 1.2 \times 10^{15}\ \text{sec}^{-1}$$

The frequency of the impinging radiation:

$$\nu = c/\lambda = \frac{3 \times 10^{10}\ \text{cm sec}^{-1}}{2000 \times 10^{-8}\ \text{cm}} = 1.5 \times 10^{15}\ \text{sec}^{-1}$$

We can write:

$$v^2 = \frac{2 \times h(\nu - \nu_0)}{m}$$

$$= \frac{2 \times 6.63 \times 10^{-27}\ \text{erg sec} \times (1.5-1.2) \times 10^{15}\ \text{sec}^{-1}}{9.1 \times 10^{-28}\ \text{gm}}$$

$$= 44 \times 10^{14}\ \text{cm}^2\ \text{sec}^{-2}\ (\text{remember } 1\ \text{erg} = 1\ \text{gm cm}^2\ \text{sec}^{-2})$$

Thus $v \simeq 7 \times 10^7\ \text{cm sec}^{-1}$

Problem: Calculate the velocity of the hydrogen electron in the first and the second Bohr orbits.

We know: $mvr = nh/2\pi$ whence $v = n\,(h/2\pi)\,(1/mr)$
and $r = n^2h^2/(4\pi^2 me^2) = n^2 a_0$ where a_0, the first Bohr radius is $h^2/(4\pi^2 me^2) = 0.529\ A$

Therefore for the first Bohr radius the velocity is:

$$v = n\,(h/2\pi)\,(1/mr) = n(h/2\pi)\,(1/ma_0)$$

$$= (1)\,\frac{6.623 \times 10^{-27}\ \text{erg sec}}{2(3.14)} \times \frac{1}{(9.107 \times 10^{-28}\ \text{gm})\,(0.529 \times 10^{-8}\ \text{cm})}$$

$$= 2.188 \times 10^{8}\ \text{cm sec}^{-1}$$

For the second Bohr radius the velocity is:

$$v = (2)\,\frac{6.623 \times 10^{-27}\ \text{erg sec}}{2(3.14)} \times \frac{1}{(9.107 \times 10^{-28}\ \text{gm})\,(2^2 \times 0.529 \times 10^{-8}\ \text{cm})}$$

$$= 1.094 \times 10^{8}\ \text{cm sec}^{-1}$$

Problem: The velocity of an electron is 2×10^{8} cm sec^{-1}. Find its wave length.

We know from de Broglie relation that $\lambda = h/(mv)$. Putting the given values and remembering that 1 erg = 1 gm cm^2 sec^{-2}

we have
$$\lambda = \frac{6.6 \times 10^{-27}\ \text{erg sec}}{9.1 \times 10^{-28}\ \text{gm} \times 2 \times 10^{8}\ \text{cm sec}^{-1}}$$

$$= \frac{6.6 \times 10^{-27}\ \text{gm cm}^2\ \text{sec}^{-2}\ \text{sec}}{9.1 \times 10^{-28}\ \text{gm} \times 2 \times 10^{8}\ \text{cm sec}^{-1}} = 3.6 \times 10^{-8}\ \text{cm}$$

Page 46. After the first paragraph

An alternate classification of the chemical elements in A and B subgroups in the Long Form of the Periodic Table:

Some authors have included the first two rows of eight elements in IA, IIA, IIIA, IVA, VA, VIA, VIIA and VIIIA Groups as shown below:

Groups :	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
							H	He
Elements :	H							
	Li	Be	B	C	N	O	F	Ne
	Na	Mg	Al	Si	P	S	Cl	Ar
	K	Ca						

After calcium begins the first series of transition elements namely scandium to copper. Since these elements are so very different from the above mentioned representative non-transition elements a series of B sub-groups namely IIIB, IVB, VB, VIB, VIIB, VIIIB, IB and IIB have been introduced:

IIIB	IVB	VB	VIB	VIIB	VIIIB	IB	IIB
Sc	Ti	V	Cr	Mn	Fe, Co, Ni	Cu	Zn

TABLE 2.4A. *Long Form Periodic Table of the Elements with a changed classification into A and B sub-groups*

Period	Gr. IA	Gr. IIA	Gr. IIIB	Gr. IVB	Gr. VB	Gr. VIB	Gr. VIIB			Gr. VIIIB	Gr. IB	Gr. IIB	Gr. IIIA	Gr. IVA	Gr. VA	Gr. VIA	Gr. VIIA	Gr. VIIIA
Period I	H 1																H 1	He 2
Period II	Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	He 10
Period III	Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
Period IV	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe, 26	Co, 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Period V	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru, 44	Rh, 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Period VI	Cs 55	Ba 56	La* 57	Hf 72	Ta 73	W 74	Re 75	Os, 76	Ir, 77	Pt 78	Au 79	Hg 80	Te 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Period VII	Fr 87	Ra 88	Ac** 89															
*Lanthanides			Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71		
**Actinides			Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lw 103		

If we persist with this approach to the A and B subgroups we have the new look Long Form Periodic Table as depicted in Table 2.4A. In the previous Long Form Table (Table 2.4) we have a continuous stretch of the A subgroups from IA to VIIA just before group VIII and on the right of group VIII we have only the B subgroups—from IB to VIIB. In the opinion of the present author this older view and classification are easier to follow than the one being piloted by some authors recently. In the alternate approach IA and IIA are followed by B subgroups from IIIB to VIIB. After group VIIIB we have IB and IIB and then the A subgroups IIIA, IVA, VA, VIA, VIIA and VIIIA. The only commendable feature of this new Table is that all the transition elements appear as members of B subgroups only from IIIB to IB through VIIIB. This alternate system of naming the groups is more cumbersome and has not been followed in Part II of this book.

Page 87. *After twentyeighth line:*

For one mole of a compound having univalent ions (like NaCl) the above relation will have to be multiplied by the Avogadro number *N* so that the lattice energy, *U*, for one mole of a uni-univalent ionic compound takes the form:

$$U = -\frac{NAe^2}{r_0}\left(1 - \frac{\rho}{r_0}\right)$$

Page 87. *Thirtysecond line; after 'a small compressibility'*:

For NaCl *A* has a value 1.747 and r_o is 2.82A. A common value of ρ alkali halides is 0.345 A so that ρ/r_o comes close to 0.1. When charges are expressed in *esu* and distances in cm., lattice energy comes out in ergs which can be changed to Kcal/mole or kJ/mole (1 erg $= 2.39 \times 10^{-8}$ cal) For NaCl such a calculation provides a value of -180 Kcal/mole as the lattice energy.

Page 88. *Section* 5.1.2. *after first para.*

Born-Haber cycle provides a value of the thermodynamic heat of formation of an ionic compound from a consideration of the lattice energy of the compound and the ionisation potential, electron affinity, heats of dissociation and sublimation of the constituent elements.

Page 109. *At the end of section* 5.2.10

6. For the pair: niobium and tantalum in Group VA of the Periodic Table the charge and the radius of the two pentavalent ions are the same (i.e. $+5$ and 0.7 *A*). Hence the ionic potentials for both the elements are the same. This explains why these two elements are so close in their chemical properties and hence so difficult to separate from each other. Similar is the case with the pair zirconium and hafnium of Group IVA (charge $+4$; radius of $+4$ ions $= 0.8$ *A*).

Page 123. *At the end of the third paragraph*

It is of interest to note the following cation/anion radius ratio for the three important geometries discussed above:

geometry	*cation/anion ratio* (r^+/r^-)
cubic	0.732
octahedral	0.414
tetrahedral	0.225

We may conclude that for the same given anion size (i.e. the same r^-) the size of the holes i.e. r^+ should vary in the order:

cubic > octahedral > tetrahedral

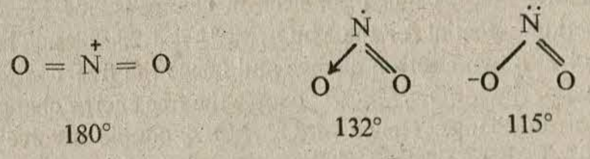
Page 131. *At the end*

Problem: Explain the bond angles in the series $\overset{+}{N}O_2$ (180°), (NO_2 (132°) and NO_2^- (115°).

The structure of $\overset{+}{N}O_2$ involves a coordinate link from nitrogen to one oxygen and a double bond to the other oxygen. This means that nitrogen has a total of $4 + 2 = 6$ electrons i.e. three pairs. Of these three pairs one is a pi bond while the other two are sigma. Pi bond does not influence the shape of a molecule or ion. So in order to minimise repulsion the two sigma bonds should ideally be at 180° i.e. the ion should be linear. Alternatively and more simply we may assume the two oxygens to be doubly bonded to nitrogen. Each double bond would then be made up of one sigma bond and a pi bond. The valence shell of nitrogen will then have $4 + 2 + 2 = 8$ electrons. Since the pi bonds do not influence the shape the two sigma bonds will prefer to stay at 180° in order to minimise repulsion thus giving a linear geometry.

In neutral NO_2 we cannot but assume a valence shell of $5 + 0 + 2 = 7$ electrons around nitrogen. This would mean three electron pairs plus a lone electron. Of the three electron pairs one is a coordinate link to one oxygen and the other two make a double bond (sigma and pi) to the other oxygen. Two bond pairs ideally should give a linear geometry. However the lone electron has some repulsive effect on the other two pairs and hence the bond angle is much less than 180°—in fact it is 132°.

In NO_2^- the negative sign i.e. an extra electron is assumed to be located on one oxygen by virtue of the greater electronegativity of oxygen. The valence shell of nitrogen is made up of $5 + 1 + 2 + 2 = 8$ electrons. This means four electron pairs: a single shared pair bond with the mononegative oxygen, a double bond to the other oxygen and a lone pair. Leaving aside the pi bond we have three electron pairs: two bond pairs and one lone pair. Because of strong repulsion by the lone pair the angle between the two bond pairs further shrinks from the ideal 120°, actually showing 115°.



Page 155. *At the end of section* 7.8.5

7.8.6. Computation of Reduction Potentials and Some Related Problems :

The relation between standard free energy change and the reduction potential is given by:

$$\triangle G^\circ = -nFE^\circ$$

In other words we can say that standard reduction potentials are the negative free energy change per electron. In computing reduction potential for a particular new and unlisted half reaction from two separate half reactions one has to find out the standard free energy change (in electron volts) for the different stages and then calculate the overall one-step reaction taking into consideration the number of electrons involved. For a given couple the free energy change in electron volts is obtained by multiplying the standard potential by the number of electrons. For example, the two half reactions of Au^+/Au and Au^{3+}/Au^+ and their reduction potentials are given below:

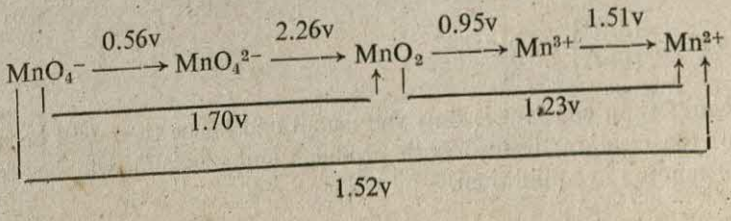
$$Au^+ + e \rightleftharpoons Au \;; \quad E^\circ = 1.7 \text{ volts}$$
$$Au^{3+} + 2e \rightleftharpoons Au^+ \;; \quad E^\circ = 1.4 \text{ volts}$$

What then will be the reduction potential of the reaction:

$$Au^{3+} + 3e \rightleftharpoons Au \;; \quad E^\circ = ?$$

The free energy change of the Au^+/Au half reaction is 1.7 *ev* while that of the Au^{3+}/A^+ is $2 \times 1.4 = 2.8$ *ev* since two electrons are involved. We add these free energy changes to get a value of 4.5 *ev* as the free energy change of the Au^{3+}/Au half reaction. Hence the standard reduction potential for the Au^{3+}/Au is 4.5/3 i.e. 1.5 volts since the $Au^{3+} \rightarrow Au$ is a three electron reduction.

In the light of the above discussion it is interesting to investigate the following redox couples in the $Mn^{2+}/Mn^{3+}/MnO_2/MnO_4^{2-}/MnO_4^-$ series:



The Mn^{3+}/Mn^{2+} and MnO_2/Mn^{3+} are both one-electron changes. Hence the free energy changes of these steps are 1.51 *ev* and 0.95 *ev* respectively. Their sum is 2.46 *ev*. Hence the free energy change per electron change is $2.64/2 = 1.23$ *ev*. So the standard reduction potential for the MnO_2/Mn^{2+} is 1.23 volts. The MnO_4^{2-}/MnO_2 couple involves a two electron change and hence the free energy change is $2 \times 2.26 = 4.52$ *ev*. For the MnO_4^-/MnO_4^{2-} couple the free energy change is 0.56 *ev* as it is a one-electron change. Hence MnO_4^-/MnO_2 couple involves a $4.52 + 0.56 = 5.08$ *ev* for a three electron change. Therefore the standard reduction potential for this couple is $5.08/3 = 1.7$ volts. The total free energy change for the MnO_4^-/MnO_2 and the MnO_2/Mn^{2+} couples are $5.08 + 2.46 = 7.54$ *ev*. Hence the standard free energy change per electron change is $7.54/5 = 1.51$ *ev*. So the standard reduction potentials for the MnO_4^-/Mn^{2+} is given by 1.51 volts.

Problem: Consider the following reduction potentials:

$$Cu^{2+} + 2e \rightleftharpoons Cu \; ; \qquad E^\circ = 0.337 \text{ volts}$$

$$Zn^{2+} + 2e \rightleftharpoons Zn ; \qquad E^\circ = -0.763 \text{ volts}$$

and ascertain whether the following reaction will go to completion:

$$Zn(s) + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu(s)$$

The E° of the above reaction is $0.337-(-0.763) = 1.1$ volts. The number of electrons involved i.e. $n = 2$.

$$\therefore \log K = \frac{nE^\circ}{0.059} = \frac{2 \times (1.10)}{0.059} = 37; \quad K = 10^{37}$$

Thus $K = \dfrac{[Zn^{2+}]}{[Cu^{2+}]} = 10^{37}$

The equilibrium constant being very large it is certain that the reaction between Cu^{2+} ions and metallic zinc will go to completion.

Problem: Consider whether the reaction between Sn(s) and Pb(II) ions will go to completion (Pb^{2+}/Pb, -0.126 volts; Sn^{2+}/Sn, -0.136 volts).

$$Sn(s) + Pb^{2+} \rightleftharpoons Sn^{2+} + Pb(s)$$

$$Pb^{2+} + 2e \rightleftharpoons Pb \; ; \qquad E^\circ = -0.126 \text{ volts}$$

$$Sn^{2+} + 2e \rightleftharpoons Sn \; ; \qquad E^\circ = -0.136 \text{ volts}$$

The E° of the above reaction is 0.01 volts; $\log K = \dfrac{2 \times (0.01)}{0.059} = 0.3$

Therefore $K = \dfrac{[Sn^{2+}]}{[Pb^{2+}]} = 2$

The equilibrium constant is thus very small and hence there will be no completion of the reaction; instead both products and reactants will be found in significant amount in equilibrium.

Problem: The standard reduction potentials of Cu^{2+}/Cu and Cu^{+}/Cu are 0.337 and 0.521 volts respectively. Calculate the standard potential of the half reaction:

$$Cu^{2+} + e \rightleftharpoons Cu$$

$$\begin{tikzcd} Cu^{2+} \arrow[r] \arrow[rr, bend left, "0.337 \text{ volts}"] & Cu^{+} \arrow[r] \arrow[r, bend right, "0.521 \text{ volts}"'] & Cu \end{tikzcd}$$

The free energy change for Cu^{2+}/Cu is 2×0.337 *ev* as it is a two-electron change. But that for Cu^{+}/Cu is 0.521 *ev*. Hence the free energy change for Cu^{2+}/Cu reaction is $2 \times 0.337 - 0.521 = 0.153$ *ev*. Since this is a one-electron change the standard potential should be 0.153 volts.

Problem: The standard reduction potentials for the half reactions (a) $Sn^{2+} + 2e \rightleftharpoons Sn$ and (b) $Sn^{4+} + 2e \rightleftharpoons Sn^{2+}$ are -0.136 volts and 0.15 volts respectively. Calculate the reduction potential of the reaction $Sn^{4+} + 4e \rightleftharpoons Sn$ and comment on the ease of reducing Sn^{2+} to Sn and Sn^{4+} to Sn.

The free energy changes of reactions (a) and (b) are -0.272 *ev* and 0.30 *ev* respectively. So the free energy change for the reaction

$$\begin{tikzcd} Sn^{4+} \arrow[r, "0.15 \text{ volts}"'] \arrow[rr, bend left, "-0.136 \text{ volts}"] & Sn^{2+} \arrow[r] & Sn \end{tikzcd}$$

$Sn^{4+} + 4e \rightleftharpoons Sn$ will be $0.30 - 0.272 = 0.028$ *ev*. Since the reaction is a four-electron change the standard reduction potential is $0.028/4 = 0.007$ volts. So we have:

$$Sn^{2+} + 2e \rightleftharpoons Sn; \qquad E^\circ = -0.136 \text{ volts}$$

$$Sn^{4+} + 4e \rightleftharpoons Sn; \qquad E^\circ = 0.007 \text{ volts}$$

It is evident that E° is negative for the couple Sn^{2+}/Sn while it is positive for the Sn^{4+}/Sn. This means that of the two couples Sn^{4+} is a stronger oxidant than Sn^{2+}. In other words metallic tin has a greater tendency to lose electrons to generate Sn^{2+} rather than Sn^{4+}. Hence Sn^{2+} will be more difficult to be reduced to tin than Sn^{4+}. It is therefore easier to oxidise Sn metal to Sn^{2+} than to Sn^{4+}.

Problem: From the reduction potentials of the following sequence of reactions predict whether MnO_4^- or MnO_4^{2-} is the better oxidant if the reduction product is Mn^{2+}.

$$MnO_4^- \xrightarrow{0.564 \text{ volts}} MnO_4^{2-} \xrightarrow{2.26 \text{ volts}} MnO_2 \xrightarrow{0.95 \text{ volts}} Mn^{4+} \xrightarrow{1.51 \text{ volt}} Mn^{2+}$$

The net free energy change for the MnO_4^{2-}/Mn^{2+} couple is:

$$2 \times 2.26 + 0.95 + 1.51 = 6.98 \text{ } ev$$

Since the couple involves a four electron change the standard reduction potential is 6.98/4 = 1.74 volts. Similar calculation for a five-electron change in the couple MnO_4^-/Mn^{2+} gives 1.5 volts as the reduction potential. Since the reduction potential for the MnO_4^{2-}/Mn^{2+} is more positive that that of the couple MnO_4^-/Mn^{2+} couple MnO_4^{2-} will be the better oxidant.

Problem: The standard reduction potentials of the Ni^{2+}/Ni and Co^{2+}/Co are −0.25 volts and −0.277 volts. Calculate the equilibrium constant of the reaction:

$$Ni^{2+} + Co \rightleftharpoons Ni + Co^{2+}$$

and hence draw reasonable conclusion.

The half reactions involved are:

$$Ni^{2+} + 2e \rightleftharpoons Ni; \qquad E^\circ = -0.25 \text{ volts}$$

$$Co \rightleftharpoons Co^{2+} + 2e; \quad E^\circ = +0.277 \text{ volts}$$

The E° of the overall reaction is 0.027 volts. The reaction involves two electrons and hence the equilibrium constant is:

$$\log K = \frac{nE^\circ}{0.059} = \frac{2 \times 0.027}{0.059} = 0.915$$

Therefore $K = 8.22$

$$\text{In the reaction } K = \frac{[Ni_s]\,[Co^{2+}]}{[Ni^{2+}]\,[Co_s]} = \frac{[Co^{2+}]}{[Ni^{2+}]}$$

Since the equilibrium constant is low not much Ni^{2+} is expected to be reduced by metallic cobalt.

Problem: From the reduction potentials of the following two half reactions:

$$Fe^{2+} + 2e \rightleftharpoons Fe \ ; \qquad E^\circ = -0.44 \text{ volts}$$

$$Fe^{3+} + 3e \rightleftharpoons Fe \ ; \qquad E^\circ = -0.036 \text{ volts}$$

determine the reduction potential of the half reaction:

$$Fe^{3+} + e \rightleftharpoons Fe^{2+}$$

The free energy change for the couple Fe^{2+}/Fe and Fe^{3+}/Fe are 2×0.44 = 0.88 *ev* and 3×0.036 = 0.108 *ev* respectively.

$$\begin{tikzcd}
Fe^{3+} \arrow[r] \arrow[rr, bend right, "-0.036\text{ volts}"'] & Fe^{2+} \arrow[r, "0.44\text{ volts}"] & Fe
\end{tikzcd}$$

Therefore the free energy change for the couple Fe^3/Fe^{2+} is 0.88−0.108 = 0.772 *ev*. Since this couple involves a one-electron change the reduction potential is 0.772 volts.

One may wonder that in section 7.8.2 while calculating the cell potential of a complete cell out of the combination of two half cells we did not bother to go through the conversion of the potential to free energies and then again to potentials. In deriving the overall cell potential we simply subtract the less positive (or more negative) potential from the more positive (or less negative) potential. In these computations the overall cell reaction is balanced i.e. one half cell reaction accepts the same number of electrons as released by the other half cell reaction. Since the number of electrons involved is the same for both the half reactions as well as the overall reaction this number will cancel out during any conversion to free energy and hence we need not bother about the conversion in the calculation of a cell potential from two standard half cells.

Page 166. *After the third paragraph*

Hard acid—hard base may interact by strong ionic forces. Hard acids have small acceptor atoms and positive charge while the hard bases have small donor atoms but often with negative charge (eg: F^-, OH^-). Hence a strong ionic interaction will lead to a hard acid-hard base combination. On the other hand a soft acid—soft base combination is mainly a covalent interaction. Soft acids have large acceptor atoms, are of low positive charge and contain unshared pair of electrons in their valence shell. Because of this ionic bonding involving soft acid hard base will be weak. Basic atoms such as oxygen (in say OH^-) and fluorine (in F^-) could form π-bond by donating electrons from their filled $p\pi$ orbitals to an empty *d*-orbital of a metal ion. It is understandable that there is likely to be a repulsion between a soft acid and a hard base because both have filled orbitals. However when a hard base is substituted by a soft base a good soft acid-soft base interaction takes place because of favourable $L \rightarrow M$ σ bond and a $M \rightarrow L$ π bond (cf. bonding in $Ni(CO)_4$).

Page 187. *After third line*

Problem: $1M$ HCl solution is gradually diluted by water till a concentration of 1×10^{-8} M is reached. What is the pH of this very dilute acid (?) solution?

If we apply the simple pH relation $pH = -\log [H^+]$ we have $pH = 8$ as our answer. But this is grossly wrong because this answer means the solution has turned alkaline which it is not. We have not added any $[OH^-]$ ion at all. Where then have we gone wrong?

We have overlooked the dissociation of the diluting medium water itself. We know: $[H^+] \times [OH^-] = 10^{-14} = K_w$

In pure water $[H^+]$ is no more than $10^{-7}M$. The acid in the problem is of the order of $10^{-8}M$ i.e. of even weaker concentration than that of pure water. So it is now evident that the pH of the above solution cannot exceed 7, that of water itself. Calculations also will prove the point.

$$H_2O \rightleftharpoons H^+ + OH^-$$

$[H^+]$ in HCl $\quad 1 \times 10^{-8}M$

$[H^+]$ from dissociation of water $\quad x \quad x$

Overall $[H^+]$ $(1\times10^{-8}+x)\,M$

$Kw=(1\times10^{-8}+x)\,x=1\times10^{-14}$

If we solve the equation $x^2+1\times10^{-8}\,x-1\times10^{-14}=0$ for x we will have a value close to $10\times10^{-8}\,M$ so that overall $[H^+]$ will be $11\times10^{-8}M$ i.e. $1.1\times10^{-7}M$. Thus we see the pH of the very dilute acid medium will be close to 7.

Problem: 1*M* NaOH is gradually diluted with water to reach a concentration of $1\times10^{-10}\,M$. What is the pH of the solution?

An impulsive answer may be that the pOH of the solution being 10 the pH should be 14−10 = 4. Instead of being alkaline the solution turns out to be acid! Once again we have overlooked the dissociation of water. Pure water has a OH^- concentration of $10^{-7}M$. The $[OH^-]$ arising out of the dilution is even weaker than that of pure water.

Hence there can hardly be any change in the pH of the solution. Calculation will also show that.

$$H_2O \rightleftharpoons H^+ + OH^-$$

$[OH^-]$ from dilute alkali $1\times10^{-10}M$

$[OH^-]$ from dissociated water x $\therefore\ [H^+]=x$

total $[OH^-]$ $(1\times10^{-10}+x)\,M$

Then $x\,(1\times10^{-10}+x)=10^{-14}=K_w$

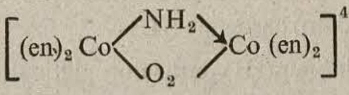
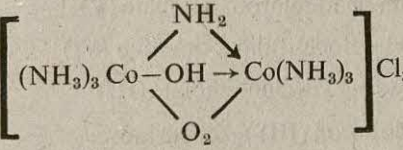
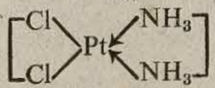
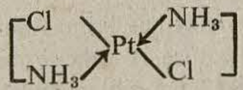
$$x^2+1\times10^{-10}\,x-10^{-14}=0$$

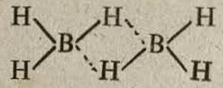
Solving the above equation for x we have close to $10^{-7}M$. Thus $[OH^-]$ is 10^{-7} so that pOH is 7. Hence pH is $14-7\simeq7$.

Page 210. *At the end of section* 10.6

Given below is a long list of examples of chemical formulas of coordination complexes alongwith their naming as per rules of latest nomenclature.

1.	$Na_3[Ag(S_2O_3)_2]$	Sodium bis (thiosulphato)argentate (I)
2.	$K[AgF_4]$	Potassium tetrafluoroargentate (III)
3.	$K_2[NiF_6]$	Potassium hexafluoronickelate (IV)
4.	$K[CrOF_4]$	Potassium tetrafluorooxochromate (V)
5.	$(NH_4)_2[VO(C_2O_4)_2]$	Ammonium bis (oxalato)oxovanadate (IV)
6.	$NH_4[Cr(NCS)_4(NH_3)_2]$	Ammonium diamminetetrakis(isothiocyanato) chromate (III)
7.	$Na_2[Fe(CN)_5(NO)]$	Sodium nitrosylpentacyanoferrate (II)
8.	$Na[Co(CO)_4]$	Sodium tetracarbonylcobaltate (−I)
9.	$K_2[Pt(NO_2)_4]$	Potassium tetranitroplatinate(II)

10.	$[Co(NO_2)_3(NH_3)_3]$	Triamminetrinitrocobalt(III)
11.	$[Co(NCS)(NH_3)_5]Cl_2$	Pentammineisothiocyanatocobalt (III) chloride
12.	$[(NH_3)_5Cr{-}OH \rightarrow Cr(NH_3)_5]Cl_5$	Pentamminechromium (III)—μ-hydroxo-pentamminechromium(III) chloride
13.	$[(NH_3)_5Fe{-}CN \rightarrow Co(CN)_5]$	Pentammine iron (III)-μ-cyano-pentacyanocobalt (III)
14.		Bis(ethylenediamine)cobalt(III)-μ-amido-μ-peroxobis(ethylenediamine)cobalt(IV) ion
15.		Triamminecobalt (III)-μ-amido-μ-hydroxo-μ-peroxo triamminecobalt (IV chloride
16.		*cis*-Diamminedichloroplatinum(II)
17.		*trans*-Diamminedichloroplatinum(II)
18.	$[Ni(PCl_3)_4]$	Tetrakis(phosphorustrichloride)nickel (O)
19.	$[Re(CO)_3(py)_2Cl]$	Tricarbonyldipyridinechlororhenium (I)
20.	$[Re(CO)_3(py)_2]$	Tricarbonyldipyridinerhenium(0)
21.	$[Au(C_2H_5)_2(en)]Br$	Ethylenediaminediethylgold (III) bromide
22.	$[Co(Br)(NCS)(en)_2]^+$	Bis(ethylenediamine)bromo(isothiocyanato) cobalt (III) ion
23.	$K_4[Ni(CN)_4]$	Potassium tetracyanonickelate (0)
24.	$K_4[Os(CN)_6]$	Potassium hexacyanoosmate (II)
25.	$K_3[Mn(CN)_6]$	Potassium hexacyanomanganate (III)
26.	$H_3[Mn(CN)_6]$	Hexacyanomanganic (III) acid Hydrogen hexacyanomanganate (III)
27.	$H_4[Mo(CN)_8]$	Hydrogen octacyanomolybdate (IV) Octacyanomolybdic (IV) acid
28.	$K[Pt(C_2H_4)Cl_3]$	Potassium ethylenetrichloroplatinate (II)
29.	$[Pt(Et_3N)Cl_3]^-$	Triethylaminetrichloroplatinate (II) ion
30.	$[Co(en)_2(NO_2)Cl]^+$	Bis(ethylenediamine)chloronitrocobalt (III) ion
31.	$[Cu(NH_3)_4][CuCl_4]$	Tetramminecopper (II) tetrachlorocuprate (II)

32. $[Co(NH_3)_4(NO_2)Cl]$ $[Au(CN)_2]$	Tetramminechloronitrocobalt (III) dicyanoaurate (I)
33. $[Co(NH_3)_5(SO_4)]_2$ $[Zn(OH)_4]$	Pentamminesulphatocobalt (III) tetrahydroxozincate (II)
34. $[Co(NH_3)_4(CO_3)]_3$ $[Fe(CN)_6]$	Tetramminecarbonatocobalt (III) hexacyano ferrate (III)
35. $[Cr(en)_2(C_2O_4)]$ $[Cr(C_2O_4)_2(H_2O)_2]$	Bis(ethylenediamine)oxalatochromium (III) diaquobis(oxalato) chromate (III)
36. $[Pt(NH_3)_4]$ $[PtCl_4]$	Tetrammineplatinum (II) tetrachloroplatinate(II)
37. $K_2[NbOF_5]$	Potassium pentafluorooxoniobate (V)
38. $[UO_2(C_3H_7O_2)_2$	Bis(acetylacetonato)dioxouranium (VI)
39. $Li[AlH_4]$	Lithium tetrahydridoaluminate (III)
40. 	Dihydridoboron (III)-μ-dihydrido-dihydridoboron (III)

Page 230. *At the end*

The ground state in these cases is the low spin state as it has been observed that the magnetic moment increases with increase in temperature. Another example has been authenticated in the iodide salt of the complex bis (2, 6 pyridinedialdehyde hydrazone)cobalt (II) ($3d^7$). At 80°K the complex gives a moment of 1.9 B.M. which goes upto 3.7 B.M. at 337°K. Thus the low spin state is the ground state.

Page 231. *At the end of the first paragraph*

The figure 10.9 depicting the cross-over region may evoke some questions to a young mind. To begin with the low spin state is the excited state while the high spin state is the ground state. As Δ continues to increase the energies of both the states begin to fall (that of the low spin state falling more steeply), then become the same at $\Delta = P$ i.e. at the cross-over region and finally the low spin state becomes the ground state while the high spin state is the excited state. At $\Delta = O$ we have the free ion and Hund's rule of maximum spin multiplicity is obeyed. Taking the d^6 case for the free ion all the d orbitals are degenerate and energy of the highest spin multiplicity state (with four unpaired electrons) is $6E + P$ where E is the energy of each of the degenerate d orbitals and P is the pairing energy. But for the lowest spin multiplicity state (with no unpaired electrons) the energy is $6E + 3P$. Thus we see that at the start the high spin state has to be the ground state. On introducing an octahedral crystal field the high spin state has an energy $-2/5\ \Delta + P + 6E$ while the low spin state has an energy $-12/5\ \Delta + 3P + 6E$. It is reasonably assumed that P remains unchanged for a particular metal ion. So if we start increasing the crystal field strength Δ by varying the coordinating ligand (but maintaining the octahedral geometry) the energies of both the spin states will keep decreasing but that of the low spin state will fall more steeply than the high spin form. The high spin state has $-2/5\ \triangle$ for one P while the low spin form has $-4/5\ \triangle$ for each P. For further simplicity E may be taken to be zero.

Page 232. Seventh line; add after 'are the most stabilised'

In the trigonal bipyramidal stereochemistry the energy difference (δ_1) between the lowest doublet set (d_{xy}, d_{yz}) and the upper doublet set (d_{xy}, $d_{x^2-y^2}$) is usually much smaller than the energy difference (δ_2) between the set (d_{xy}, $d_{x^2-y^2}$) and the highest energy d_{x^2} orbital. It has been established that δ_1 can never exceed pairing energy P of a metal ion. But δ_2 may be less than or greater than P. Therefore in this geometry d^1, d^2, d^3 and d^4 systems will always give the high spin form while d^5, d^6, d^7 and d^8 systems may be either high spin or low spin. Hence with favourable ligands i.e. $\delta_2 \simeq P$ we may observe anomalous moments with the d^5, d^6, d^7 and d^8 systems. In reality, however, for d^8 nickel (II) alone high spin and low-spin trigonal bipyramidal complexes are known. For all the others i.e. d^5, d^6 and d^7 systems all the known trigonal bipyramidal complexes are high spin. Academically, however, the spin arrangements will be say for d^5 as:

high spin d^5 : $(d_{xz}, d_{yz})^2, (d_{xy}, d_{x^2-y^2})^2, d^1_{z^2}$

low spin d^5 : $(d_{xz}, d_{yz})^3, (d_{xy}, d_{x^2-y^2})^2, d_{z^2}$

Page 237. Last line of second paragraph and second line of fourth paragraph

Read unsymmetrical for uneven

Page 238. Seventh line from bottom

Read unsymmetrical for uneven

Page 243. At the end of the fourth paragraph

10.11.4. Some Problems Related to Crystal Field Theory

Problem: 10 Dq of $[Mn(H_2O)_6]^{3+}$ is known from electronic spectrum to be 21,000 cm^{-1}. The pairing energy of Mn(III) is 28,800 cm^{-1}. Predict whether the complex is high spin or low spin.

Mn (III) is a $3d^4$ system. The energies in the high spin and the low spin state are:

$$\underline{E_{h.s.}} = E_{t_{2g}^3 e_g^1} = -6\,Dq = -(6\times 21{,}000/10\ \text{cm}^{-1})$$

$$= -12{,}600\ \text{cm}^{-1}$$

$$\underline{E_{l.s.}} = E_{t_{2g}^4} = -16Dq + P = -(16\times 21{,}000/10\ \text{cm}^{-1})$$

$$+\,28{,}800\ \text{cm}^{-1} = -4{,}800\ \text{cm}^{-1}$$

Since the $E_{h.s.} \leqslant E_{l.s.}$ the complex will be stable in the high spin form.

Alternatively we can argue that a low spin complex is formed only when 10 *Dq* exceeds *P*. Since in this case 10*Dq* is significantly lower than *P* the hexaaquo manganese (III) complex has to be high spin.

Problem: 10*Dq* values of $[Ru(H_2O)_6]^{2+}$ and $[RuCl_6]^{3-}$ are nearly the same but according to spectrochemical series, the value for 10 *Dq* for the chloride ion should be lower than H_2O. How do you explain the similarity of the 10 *Dq* values of the two complexes?

It is true that chloride ion is a far weaker ligand than H_2O. In one of the two complexes we have ruthenium (II) associated with H_2O and in the other ruthenium (III) is associated with the weaker ligand chloride. 10 *Dq* depends on several factors of which a very important one is the oxidation state. It is an empirical fact that with an increase in the oxidation state by one unit (from $+2$ to $+3$) 10 *Dq* increases by about 100%. This explains why even a weaker ligand chloride produces with ruthenium (III) nearly the same 10 *Dq* as does hexaaquo ruthenium (II).

Problem: $[NiCl_4]^{2-}$ is tetrahedral paramagnetic while $[PdCl_4]^{2-}$ and $[PtCl_4]^{2-}$ are diamagnetic square planar.

It is a fact that oxidation state remaining the same 10 *Dq* increases significantly from the first transition series to the second and then to the third. Again as we move from nickel (II) ($3d^8$) to palladium (II) ($4d^8$) to platinum (II) ($5d^8$) the *d* orbitals extend in space accordingly. The mean distance between the *d* orbitals therefore increases in the order Ni (II) < Pd (II) < Pt (II) thus causing a substantial lowering of the pairing energy: Ni (II) > Pd (II) > Pt (II). Thus both increasing 10 *Dq* and decreasing pairing energy favour low spin complexes as we move from nickel (II) to palladium (II) to platinum (II).

Problem: Chromium (III) under forcing conditions forms $[CrCl_6]^{3-}$ but the corresponding complexes are never found in Mn (III) and Fe (III). Why?

Cr (III), Mn (III) and Fe (III) are d^3, d^4 and d^5 systems respectively. Since chloride ion is a weak field ligand all the complexes if formed at all must be high spin. The CFSE's are -12 *Dq*, -6*Dq* and 0*Dq* (in respective *Dq*'s) respectively. Hence if at all hexachloro complexes are to be formed the best chance is with chromium (III).

Problem: Why does $[Mn(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ have pale colour as compared to the complexes of other oxidation states of these metals?

Intensity of electronic transition is dictated by the extent to which the selection rules are allowed ($\triangle l = \pm 1$ and $\triangle S = 0$). Both the complexes are high spin d^5 with $t^3_{2g}\ e^2_g$. Here all electronic transitions are doubly forbidden: Laporte forbidden as they must be all *d–d* transitions ($\triangle l = 0$) and secondly these are also spin multiplicity forbidden ($\triangle S \neq 0$). We can arrange the five electrons in no more than one way maintaining the highest spin multiplicity ($2S + 1 = 6$). (cf : Fig 11.11; page 276) Hence the colours of these two complexes are so very faint.

Problem: $(NH_4)_2[VF_6]$ shows one electronic transition around 20.1 kK while $[VO(acac)_2]$ in chloroform gives three bands around 14.8, 16.8 and 25.0 kK. Explain

Both the complexes have $3d^1$ vanadium (IV). $(NH_4)_2[VF_6]$ may be viewed as octahedral with some slight Jahn Teller distortion while $[VO(acac)_2]$ is under heavy tetragonal compression (cf. Fig. 10.15). The vanadyl oxygen bond is much too short compared to the other equatorial vanadium-oxygen bonds. Hence the splitting of the *d* orbitals is unlike what obtains in octahedral complexes. So in the former compound one transition ($t_{2g} \rightarrow e_g$) is expected while in the latter as many as three ($d_{xy} \rightarrow d_{xz}, d_{yz}$; $d_{xy} \rightarrow d_{x^2-y^2}$; $d_{xy} \rightarrow d_{z^2}$) are expected. Indeed this is what is seen experimentally.

Problem: Arrange the following pairs on the basis of crystal field splitting paramaters (10 *Dq*):

(a) $[V(H_2O)_6]^{2+}$ and $[V(H_2O)_6]^{3+}$

(b) $[Fe(CN)_6]^{4-}$ and $[Os(CN)_6]^{4-}$

(a) 10 *Dq* increases with oxidation state, other factors remaining the same. In $[V(H_2O)_6]^{2+}$ vanadium is in + 2 oxidation state while in $[V(H_2O)_6]^{3+}$ the oxidation state is + 3. Hence 10 *Dq* of $[V(H_2O)_6]^{3+}$ is greater than that of $[V(H_2O)_6]^{2+}$. In fact the values of 10 *Dq* are: $[V(H_2O)_6]^{2+}$, 12.30 kK and $[V(H_2O)_6]^{3+}$, 18.6 kK.

(b) 10 *Dq* increases substantially when we move vertically downward in a group from one transition series to the next. From Fe (II) we have to traverse two transition series to come to Os (II). Hence 10 *Dq*'s will vary in the order:

$$[Os(CN)_6]^{4-} > [Fe(CN)_6]^{4-}$$

Problem: Arrange the following species in the order of increasing Jahn Teller distortion in an octahedral environment: (a) high spin Co (III) (b) low spin Co (II) (c) copper (II) and (d) Ti (III).

Jahn Teller effect becomes more severe when the e_g level is unsymmetrically occupied than when the t_{2g} level is unsymmetrically occupied. The electron arrangements are: high spin cobalt (III), $t^4_{2g}\ e_g^2$; low spin cobalt (II), $t_{2g}^6 e^1_g$; copper (II), $t^6_{2g}\ e^3_g$; titanium (III), $t^1_{2g}\ e^0_g$. So the increasing order of Jahn Teller distortion is:

$$\text{Ti (III)} \simeq \text{high spin cobalt (III)} < \text{Cu (II)} \simeq \text{low spin Co (II)}$$

Problem: $KReO_4$ is colourless whereas $KMnO_4$ is intense purple. Explain.

Both the central elements are in oxidation state + 7 and are tetrahedrally surrounded by four oxide ions. The colour is due to C—T transition of the type: ligand → metal ion. The 5*d* orbitals of Re are at a higher energy than the 3*d* orbitals of Mn. The antibonding M.O.'s of $KReO_4$ are more antibonding than those of $KMnO_4$. This means that ligand → metal C. T. transition will appear at much higher energy for $KReO_4$ than for $KMnO_4$. As the transition in $KReO_4$ appears at the near UV we see the compound as colourless. For $KMnO_4$ the transition is very much within the visible region (λ_{max} = 545 nm) and we observe a purple colour.

In keeping with these transitions it is an experimental fact that $KMnO_4$ is a better oxidising agent than $KReO_4$. In fact a low energy C.T. band (as in $KMnO_4$) indicates that requisite energy for a redox reaction involving the species is more easily available and hence a redox reaction should proceed more favourably with $KMnO_4$ than with $KReO_4$.

Problem: Hexaaquo iron (III) is nearly colourless. On the addition of potassium thiocyanate a blood red colour develops. Explain.

Iron (III) is a d^5 system. Water is a weak field ligand. Hence hexaaquo iron (III) is high spin. The *d—d* transitions in high spin d^5 complex are doubly forbidden and hence we see very weak colour. However iron (III) is an oxidant while thiocyanate ion is a reductant. So in the presence of thiocyanate ion charge transfer transition occurs (being of the ligand → metal type). C—T transition is allowed and in this particular case is very favoured so that low energy transition in the visible range takes place. Being an allowed transition the intensity is very high.

Problem: The crystal field splitting parameter, $\triangle$, of $[IrCl_6]^{3-}$ is 27,600 cm^{-1}. Convert this $\triangle$ to wave length in nm. What is your prediction about its magnetic properties?

$$\text{Wave length} = \text{inverse of wave number} = 1/(27{,}600\ cm^{-1})$$

$$= (1/27{,}600)\ cm = (1/27{,}600)\ 10^7\ nm = 362\ nm.$$

It is a general rule that $\triangle$ increases as we move from the first transition series to the second and then to the third along a particular group. Iridium(III) being a d^6 system of a third series has a comparatively low pairing energy. Hence $\triangle$ easily exceeds *P* and a low spin diamagnetic complex is likely.

Page 245. *Third line; after 'formed'*

In the case of substitution of the hexaaquo metal (II) complex by six monodentate ligands there is no net change in the number of reactant species and product species. But in the case of substitution by three bidentate chelating ligands the number of product species goes up by three (7—4 = 3) compared to the reactant species. If a sexadentate ligand were used instead of three bidentate ligands then the above difference would have been 7—2 = 5. Thus the product species have much more translational randomness than the reactant species, thus giving higher entropy.

Page 258. *After twelfth line:*

Hemoglobin is, in reality, a highly complicated system and therefore researches of the very highest order have gone to build up our current knowledge of this system. Hemoglobin, in fact, is built up of four heme (10—XXXI) units connected to a protein called globin. The complexity of the system can be guessed from its molecular weight being as high as 64,000 or so. The heme iron (II) is connected to a histidine nitrogen which forms a part of the globin protein. The sixth coordination position of iron (II) is occupied by a water molecule. Structural studies reveal that in the hemoglobin the d^6 iron (II) is high spin while in the oxyhemoglobin it is low spin. We have already learnt that in the high spin state d^6 is $t^4_{2g}\ e_g{}^2$ and hence has to have a significantly higher radius than in the low spin state $(t_{2g}{}^6)$. In view of the larger radius of high spin iron (II) it just does not fit in the hole created by the four sp^2 nitrogens of the heme ring. The result is that the iron (II) is raised by about 0.7A above the macrocyclic N_4 basal plane. But in oxyhemoglobin the iron (II) being low spin (and hence of smaller radius) fits into the N_4 basal plane. Hemoglobin is paramagnetic (4.9 B.M.) while oxyhemoglobin and carbonmonoxyhemoglobin are diamagnetic. Coordination of dioxygen (O_2) changes the iron (II) of one heme unit from the high spin state to the low spin state. This activates the other heme units of hemoglobin leading to efficient oxygen uptake. It is also of interest to note that hemoglobin takes up more oxygen at higher pH (say 7.6) than at lower pH (6.8). This effect of pH on the oxygen uptake capacity of hemoglobin is known as Bohr effect.

Closely related to hemoglobin is *myoglobin*—another heme containing protein. It may be viewed as a monomer of hemoglobin, being made up of one heme unit connected to one polypeptide chain (which is roughly one-fourth of globin). Its molecular weight is about 16,000. Myoglobin is the pigment present in the muscles. It is a better oxygen absorber than hemoglobin. Hemoglobin binds oxygen molecules in the lungs and transports them to the muscles. Since the oxygen pressure is low in the muscles hemoglobin releases oxygen to the myoglobin of the muscles. Myoglobin uses the stored oxygen as and when required during oxidation processes in the body. The CO_2, that is released by the body, is carried by the hemoglobin back to the lungs. This is believed to be achieved by $-NH_2$ group present in hemoglobin via formation of carbamino group ($-NH_2 + CO_2 \rightarrow -NHCOOH$).

Page 262. *The blocks of Fig.* 11.2 *and* 11.3 *should be read as interchanged*

Page 305. *At the end of the second paragraph*

Determination of the Decay Constant and Half life:

It is reasonably assumed that each one of the radioactive atoms of a given species emits from within its nucleus either an alpha particle or a beta particle (as the case may be) on disintegration. Hence a count of the alpha particles or the beta particles provides a reasonable estimate of the disintegration rate.

Suppose we follow the emission of the alpha particles or the beta particles over a known time interval $\triangle t$ (which may be minutes, some hours or even a day). $\triangle t$ must be a reasonable time lag but short compared to the half life of the radioelement under study. If $\triangle N$ is the number of particles recorded in a counting machine then $\triangle N/\triangle t$ will approximately represent the rate of disintegration dN/dt of equation (1). Then manipulating equation (1) we have:

$$k = \frac{\triangle N/\triangle t}{N}$$

N, which represents the total number of atoms present in the sample, can be evaluated from a knowledge of the weight of the element, its atomic weight and the Avogadro number. The weight of the element divided by the atomic weight provides the gm. atom which on multiplication by the Avogadro number (6.02×10^{23}) gives the the number of the atoms present in the sample. If the sample is a compound then the weight of the sample is to be divided by the molecular weight to get the gm. mole. This on multiplication by 6.02×10^{23} will give the actual number of radioactive atoms present in the sample.

For samples whose half lives vary from some second to some months a graphical technique making use of equation 5 is used.

Equation 5 may be manipulated as shown below:

$$\log N = \log N_0 - 0.4343\, kt$$

The rate of ejection of particles may be assumed to be proportional to the number N of the radioactive atoms present at that instant. The rate of decay is followed in a counting machine. If I_t and I_0 stand for the rates at time t and at arbitrary zero time, then the above equation may be rewritten as:

$$\log I_t = \log I_0 - 0.4343\, kt$$

Several $\log I_t$ values are determined at several time intervals and these are plotted against respective t. Normally a straight line results. The slope of this line (which is negative) is expressed in reciprocal time (second^{-1}/minutes^{-1}/hours^{-1}) The disintegration constant k is given by the slope ($-0.4343\, k$) divided by -0.4343 and is obtained in units of reciprocal time. The half life is then easily obtained by the relation given in equation 6.

A straight line plot is not obtained if the radioactive element is not pure or has some significant amount of radioactive daughters already accumulated in the sample. Determination of half life etc. then becomes quite complicated.

Page 307. *After thirteenth line*

The following Table gives us an idea as to the fraction of radioactive species of $^{210}_{83}$Bi (a beta emitter) remaining after a certain number of half life periods.

TABLE 12.3A. *Decay of* $^{210}_{83}$Bi (*half life* = 5 *days*)

Time (days)	Number of half lives	Fraction left	Fraction decayed
0	0	1.	0
5	1	$\frac{1}{2}$	$\frac{1}{2}$
10	2	$\frac{1}{4}$	3/4
15	3	1/8	7/8
20	4	1/16	15/16
$5n$	n	$(\frac{1}{2})^n$	$1-(\frac{1}{2})^n$

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